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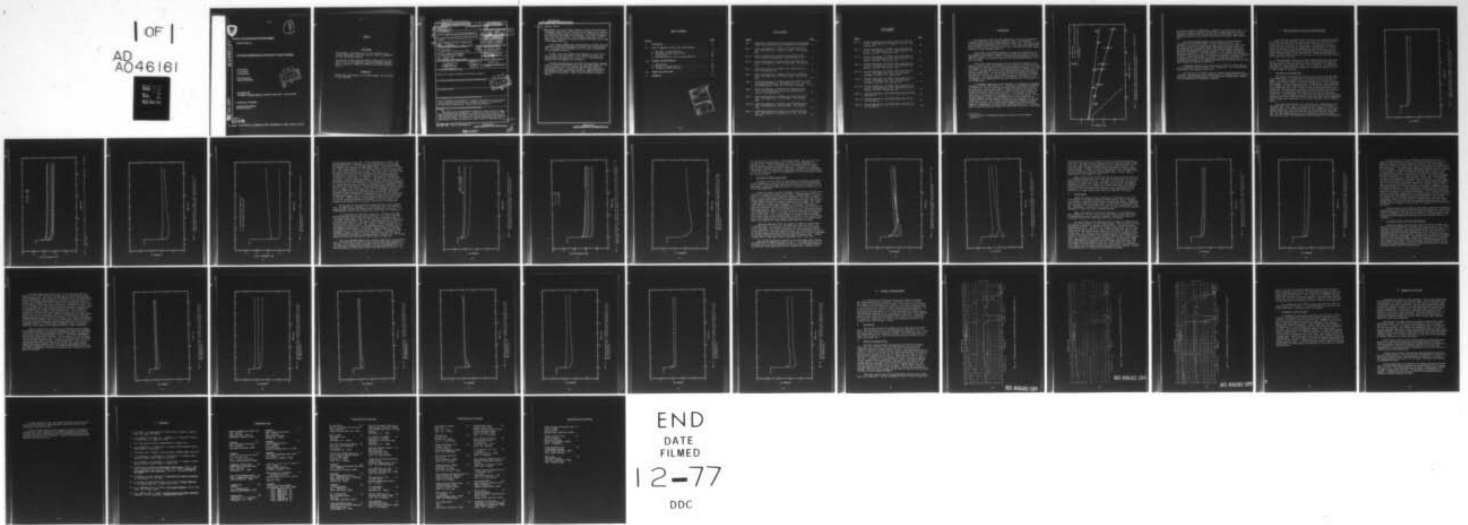
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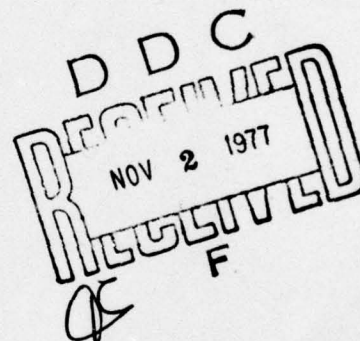
Research and Development Technical Report

ECOM-74-0030-14

LITHIUM-INORGANIC ELECTROLYTE BATTERIES

J. R. Driscoll
P. G. Gudrais
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EIC Corporation
Newton, MA 02158



OCTOBER 1977

Fourteenth Progress Report for Period 01 April 1977 — 30 June 1977

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The major area of investigation during this report period has been the voltage delay and depression in Li/SOC1 ₂ cells after storage at 710C. These are due to films on the Li anode surface which arise from reaction with the electrolyte. The effects of test-cell design have been assessed: Substitution of Teflon by quartz has a major effect in improving cell		

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20. Abstract (Cont.)

performance; cells with a small surface-to-volume ratio show better performance than those with large surface-to-volume ratios; presence of exposed Ni Exmet causes an increase in cell passivation, which is most noticeable with small area electrodes. This effect diminishes with larger area electrodes. This increased passivation is most likely due to increased Li corrosion caused by the reduction of SOCl_2 on the exposed Exmet.

Li(Ca) anodes prepared from $\text{Ca}(\text{SbCl}_6)_2/\text{SOCl}_2$ solutions show good retention of discharge performance but suffer some initial passivation. We believe this is primarily due to Fe and Cu contamination of the $\text{Ca}(\text{SbCl}_6)_2$ solution.

Li/ SOCl_2 cells were prepared with additions of 1 w/o of PCl_3 , PCl_5 or P_2S_5 to the electrolyte. Cells with PCl_3 and PCl_5 have retained good performance after 522 hr at 71°C . The effect may, however, be at the expense of Li corrosion.

Infrared spectrophotometry has shown that the hydroxy compounds found in freshly prepared electrolyte are eliminated rapidly at 71°C in the presence of Li. This reaction generates HCl , which is subsequently removed by reaction with the Li. Na_2SO_4 and $\text{Na}_2\text{S}_2\text{O}_4$ are apparently not soluble enough in SOCl_2 to make the SO_3^- and $\text{S}_2\text{O}_4^{2-}$ anions IR detectable. $\text{S}_2\text{O}_4^{2-}$ reacts with SOCl_2 to produce S and SO_2 .

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I. INTRODUCTION

In recent years there has been considerable research and development on ambient-temperature, high energy density Li cells. A particularly promising system is based on thionyl chloride, SOCl_2 (1,2). Here SOCl_2 serves both as solvent and depolarizer for the cell. D cells have delivered 100 Whr/lb and 40 W/lb at the 2.5 hr rate and, as usual, have delivered higher energy densities at lower discharge rates (3).

The purpose of the present program is to study the feasibility of an all-inorganic electrolyte Li primary battery operable and storable over the temperature range of -40°F to $+160^\circ\text{F}$. The desired energy density is 150 watt-hours per pound of total battery weight and the desired power density is 50 watts per pound.

This report contains the results of work carried out during the 14th quarter of this program. The emphasis of the program has continued to be an investigation of the problem of cell passivation during storage at 71°C (160°F). Our studies (4), and others (3,5), show that passivation is caused by the formation of a nonconductive film on the Li anode during storage, especially at elevated temperatures. Our research efforts have been directed at studying the effects of the film on cell performance and at investigating cell modifications with a view toward improved cell performance. As a result of our investigation, two promising leads have been developed for the alleviation of the voltage delay.

A remarkable improvement was obtained with cell preparation techniques designed to improve system purity (6). Although the improvement was substantial (Figure 1), the cell performance degrades after about 300 hr storage to the point where voltage delays appear.* While the data are sufficient for establishing general trends, there is sufficient scatter that rigorous comparison on a cell-to-cell basis is difficult. In an attempt to alleviate this problem, we initiated an investigation of our test cell design. In our previous quarterly report, we established that our H-cell design was an adequate sealing technique against exchange with the atmosphere for up to at least 300 hr at 71°C . As a further provision against atmospheric exchange, we are now routinely using a second sealed chamber which insures minimal danger of contamination. We also found a marked improvement in cell performance by substituting quartz plates for Teflon discs in the cell. The Teflon

*"Voltage delay" is arbitrarily defined as initial cell polarization below 2 V.

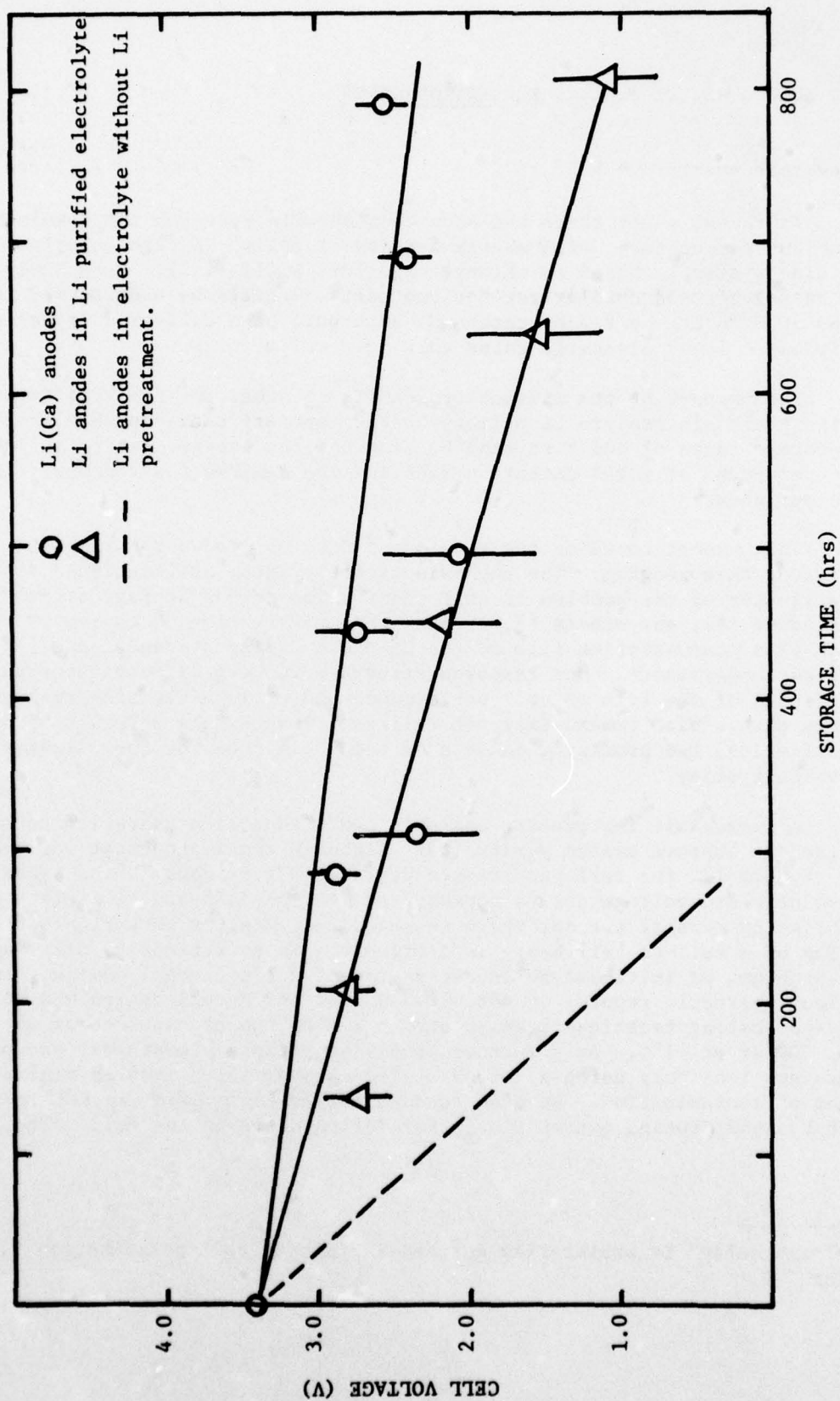


Fig. 1. Average cell voltage at 60 sec after the application of a constant load. The load will draw $\sim 7.0 \text{ mA/cm}^2$ from a fresh cell.

discs were a source of contamination leachable by the SOCl_2 electrolyte. In the previous quarterly report, we also noted an apparent effect on cell performance of electrode size and an effect due to the Ni Exmet anode screen. During this quarter we have studied these effects and present those results here.

The second promising method of alleviating the voltage delay has utilized Ca as an alloying element at the Li anode surface (7). The performance of cells utilizing the Ca-coated Li anode has been better than the pure Li anode cells prepared under high purity conditions (Figure 1). The $\text{Ca}(\text{SbCl}_6)_2$ salt appeared to offer a more efficient means of preparing the electrodes because of its high solubility ($> 1\text{M}$) compared with CaCl_2 , which has a solubility of a few mM. However, in the previous quarterly we established that the free Ca^{2+} concentration is very small in the 1M $\text{Ca}(\text{SbCl}_6)_2$ solution. Calcium does deposit on Li from this solution by exchange, but at a relatively slow rate ($\sim 0.03 \text{ coul/cm}^2/\text{hr}$). During this quarter we have prepared $\text{Li}(\text{Ca})$ anodes by the exchange technique and tested them after storage. These results are reported in Section II.

During this quarter we have also tested the effect of three additives on cell performance after storage at 71°C . These were: PCl_3 , PCl_5 and P_2S_5 . Those results are reported in Section II.

The survey of the Li/SOCl_2 system by infrared spectrophotometry was continued. The purposes of the investigation are to establish the suitability of IR for analytical measurements, and to apply the technique where feasible for the elucidation of the Li/SOCl_2 chemistry.

II. TESTS OF COMPLETE Li/SOCl₂ CELLS AFTER STORAGE

In our previous quarterly report we described the improved performance of Li/SOCl₂ test cells assembled with quartz plates substituted for Teflon discs as the cell material. We had felt that Teflon due to its porous nature might act as a source of contamination. IR spectrometry of an electrolyte solution stored with the Teflon discs confirmed this. The Teflon caused the appearance of several absorbances in the IR spectrum. One of these is due to the presence of HCl, the others are as yet unidentified but their positions between 1000 cm⁻¹ and 1300 cm⁻¹ suggest sulfur-oxygen compounds. The HCl probably arises from reaction of the SOCl₂ with H₂O contained in the Teflon pore structure.

The quartz plate cells had two other variations from the Teflon cell design. The cells had 4 cm² anodes vs. the 1 cm² in the Teflon cells and the anodes did not utilize Exmet screen current collectors. We suggested that these two changes might also affect cell performance. To explore this possibility, storage tests were carried out to isolate the effects of each of these changes in technique.

A. The Effect of Electrode Size

The studies to determine the effect of electrode size utilized three cell configurations. The quartz plate cells were used for 1 cm² and 4 cm² anodes. The anode and cathode are placed parallel to one another with a glass fiber separator between. The second configuration was also a parallel plate design. It was a multiple anode and cathode design. Three anodes and four cathodes were used. The anodes were 19.4 cm² per side giving the cell a total anode area of 116 cm². A spiral wound configuration was the third design used: Two anodes were wound with a cathode and glass fiber separator. The areas of the inside and outside anodes were 65.3 cm² and 79.8 cm², respectively. Once assembled, the cells were stored in the double sealed cells, i.e., in O-ring sealed glass inner cells and argon filled O-ring sealed aluminum outer cells. They were stored at 71°C and tested at room temperature with a constant load which draws 6.5-7.0 mA/cm² from fresh cells of similar design.

The results indicate that the 1 cm² anode cells perform better than the larger area cells. Figure 2 contains the initial cell polarization curves of three 1 cm² anode cells stored 262 hrs. Figures 3, 4 and 5 show similar curves for 4 cm² cells stored 256 hrs, for the multiple electrode parallel plate cells stored 257 hrs and for a spiral wound cell stored 255 hrs. The cell anodes did not utilize an Exmet screen current collector. The three cells with 1 cm² anodes show an initial rapid (<1 sec) polarization

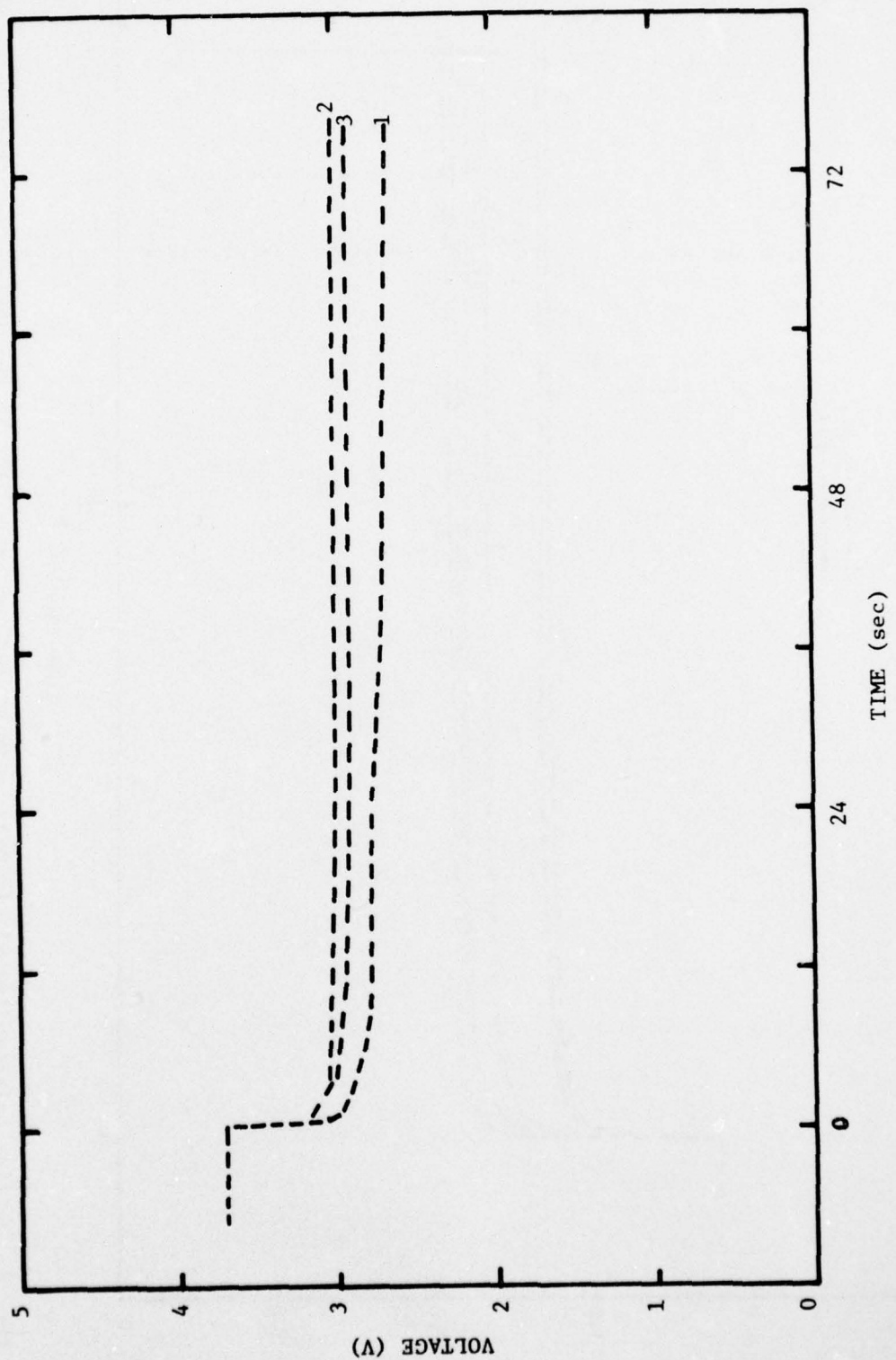


Fig. 2. Initial polarization of Li/SOCl₂ cells stored 262 hrs at 71°C. The anodes were 1 cm² with no Exmet. The load was 490Ω.

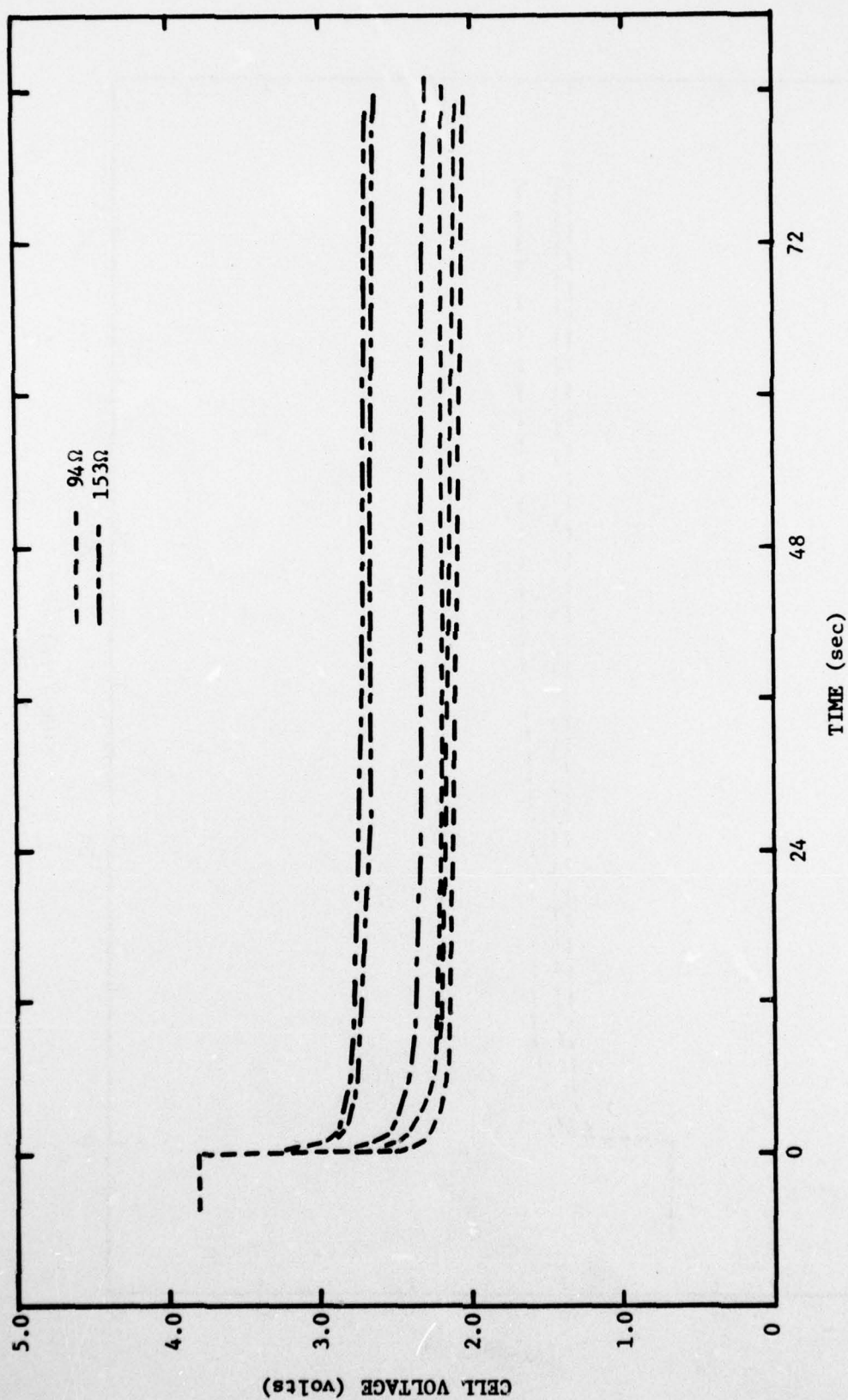


Fig. 3. Initial polarization of L1/SOCl₂ cells stored 256 hr at 71°C in the HAL configuration. The anodes were 4 cm².

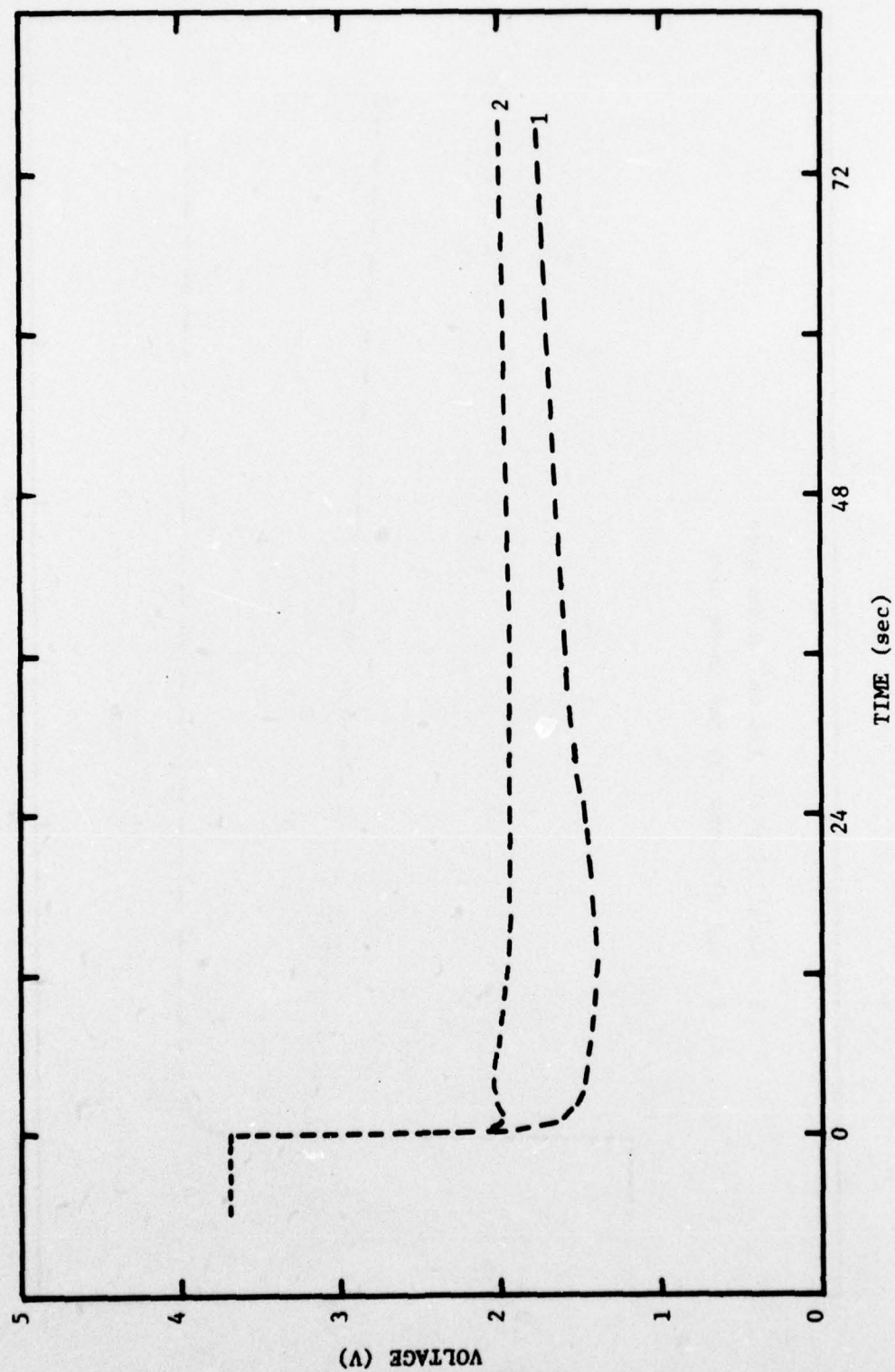


Fig. 4. Initial polarization of Li/SOCl₂ cells stored 257 hrs at 71°C. Three anodes of 6 in² each were used. The load was 4.6Ω.

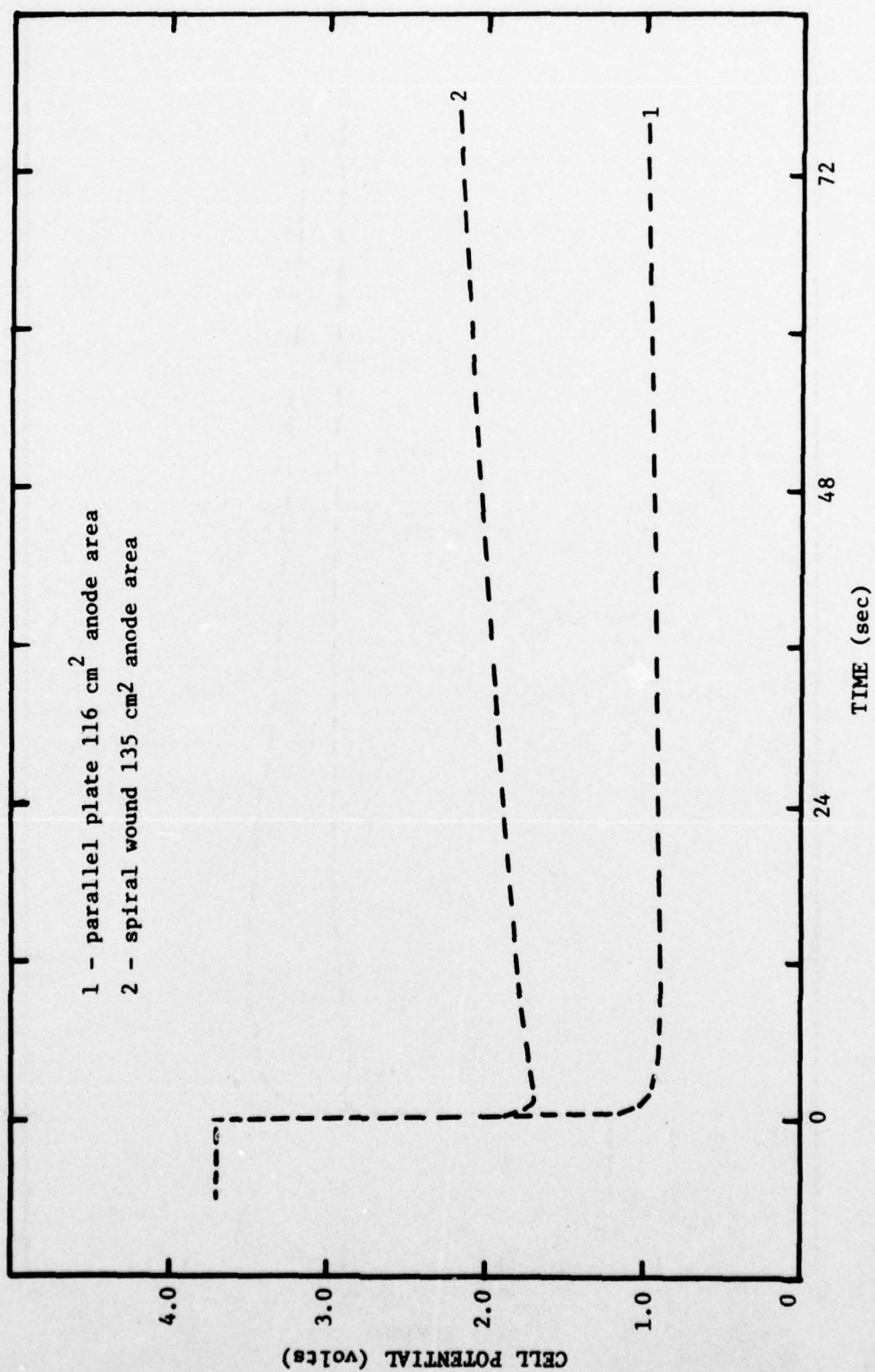


Fig. 5. Initial polarization of Li/SOCl₂ cells stored 255 hrs at 71°C.
The load was 4.6Ω.

with the application of the load. This is probably due to iR drop. The initial polarization is followed by a less rapid decline in cell voltage and, beyond 30 sec, the cell voltages remain stable. At the 60 sec point, the average current density was 5.86 mA/cm^2 , which is 84% of that of a fresh cell. The general behavior of the 4 cm^2 anode cells is similar except that the initial rapid polarization is greater. The tests on the 4 cm^2 cells used two different load resistors which bracketed the value which would give $\sim 7 \text{ mA/cm}^2$ from a fresh cell. An average of the two current densities is 4.91 mA/cm^2 , or 71% of that of a fresh cell. The data for the multiplate cells shows a slightly different behavior. Both cells show initial rapid polarization which is substantially greater than was observed with the 1 cm^2 or 4 cm^2 cells. The cell labelled No. 1 then continued to polarize gradually, the voltage passed through a minimum and continued to rise gradually for the duration of this test (~ 80 sec). The maximum and minimum are probably indicative of changes in the passivating film. The first minimum in the cell No. 2 curve is probably due to the combined effect of iR drop and concentration polarization being compensated by some breakup of the film. The second minimum is caused by concentration polarization at this freshly exposed area. The subsequent gradual rise in cell voltage is probably due to slow breakup of the film. A similar chain of events probably occurs in cell No. 1 but the initial minimum and maximum are obscured. At the 60 sec point, the average current density was 3.47 mA/cm^2 or 55% of that of a fresh cell.

The data for the spiral wound cell shows the rapid initial polarization. The magnitude is comparable to the multiplate cells. The voltage passed through a minimum and gradually rose for duration of this test. The current density of 60 sec was 3.38 mA/cm^2 or 49% of that of a fresh cell.

It is clear that for 260 hrs of storage the 1 cm^2 anode cells have better characteristics than the larger area cells. The trend is the same for longer storage times. Figure 6 shows the initial discharge curve of 1 cm^2 anode cells stored for 352 hrs. The pattern of behavior is similar to the cells stored 262 hours. The average current density at 60 sec was 5.67 mA/cm^2 or 82% of that of a fresh cell. Figure 7 contains the data for a 4 cm^2 anode cell stored 278 hrs. The discharge pattern is similar, but the performance is much inferior. The average current density at 60 sec was 3.55 mA/cm^2 or 51% of that of a fresh cell. Figure 8 contains the initial discharge curve of a spiral wound cell stored 287 hrs. The pattern of the discharge is similar to that of the cell stored 255 hrs, with the initial rapid polarization followed by a minimum and then a gradual rise. The current density at 60 sec was 2.86 mA/cm^2 or 56% of that of a fresh cell.

The clear advantage shown by the 1 cm^2 cells may be due to the relative size of the electrode in relation to the volume of electrolyte contained in the cell. In the quartz plate cell design, the cell has approximately 2.7 cc of electrolyte, contained in the cathode (1 cc) and the separators (1.7 cc). Thus the surface to volume ratio in the 1 cm^2 anode cells is 0.74 cm^{-1} . In

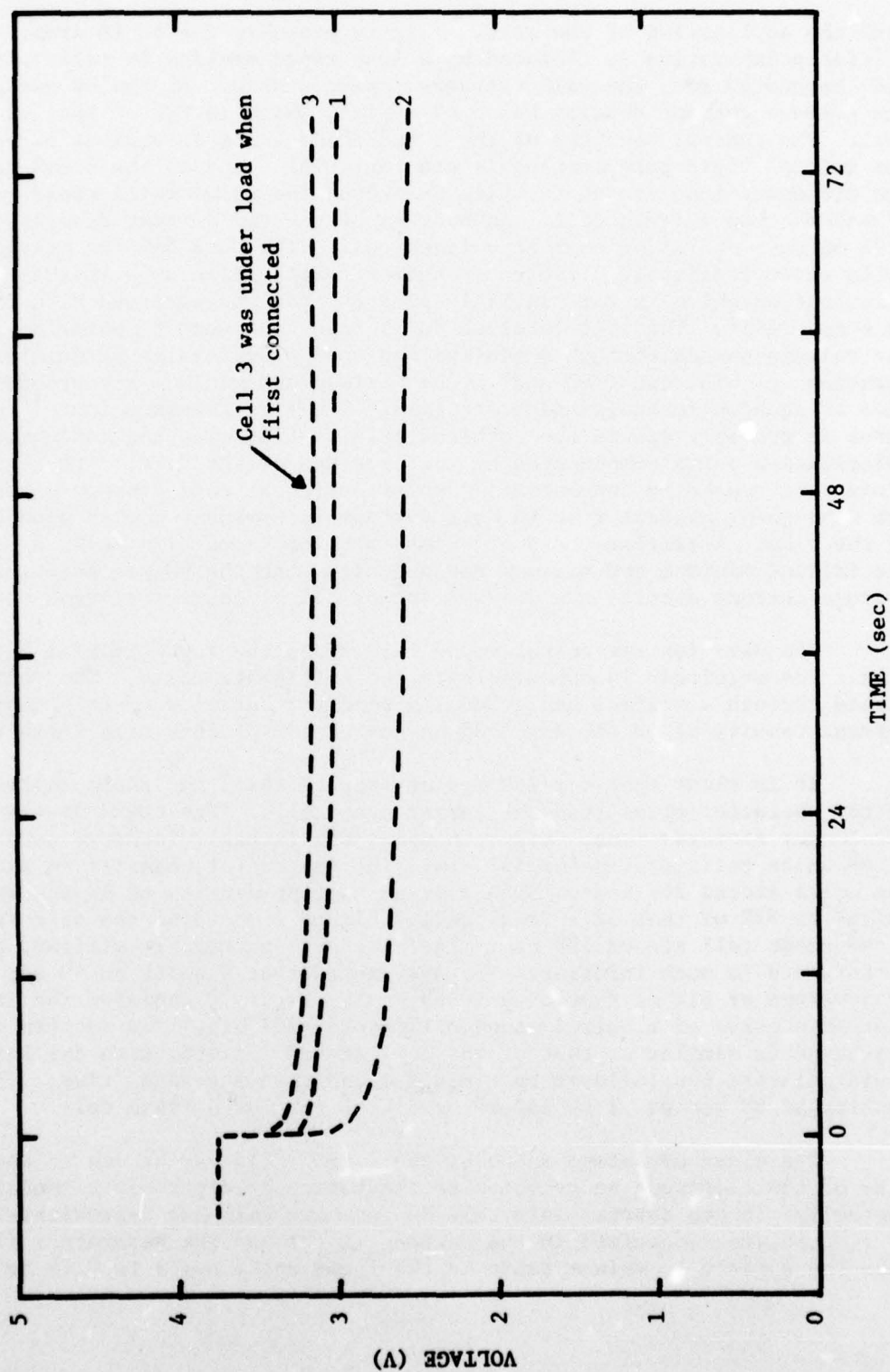


Fig. 6. Initial polarization of Li/SOCl₂ cells stored 352 hrs at 71°C. The anodes were 1 cm² with no Exmet. The load was 490Ω.

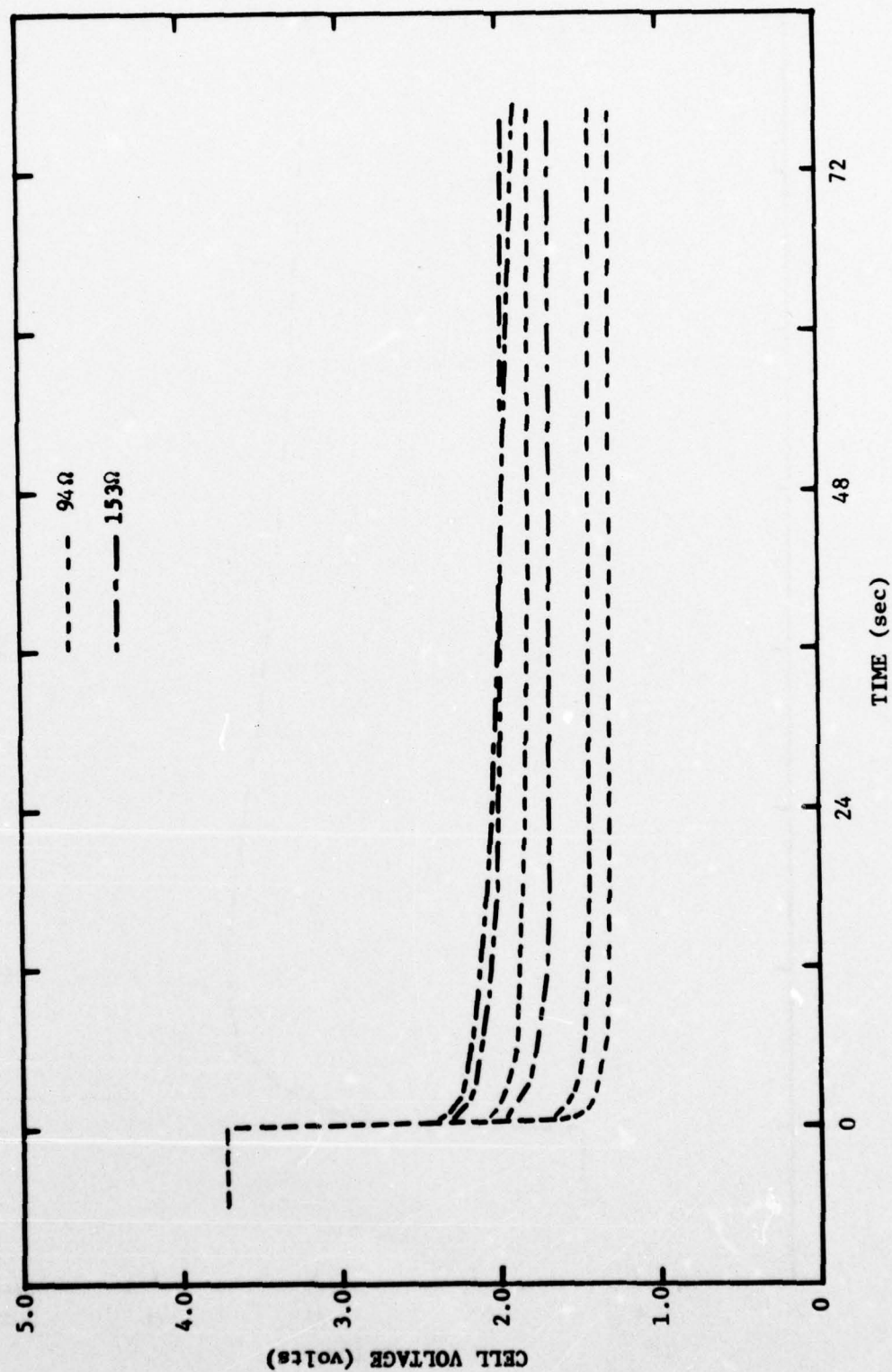


Fig. 7. Initial polarization of Li/SOCl₂ cells stored 278 hr at 71°C in the HAL configuration. The anodes were 4 cm². The cells were discharged at 1 A/cm² for 2 sec prior to storage.

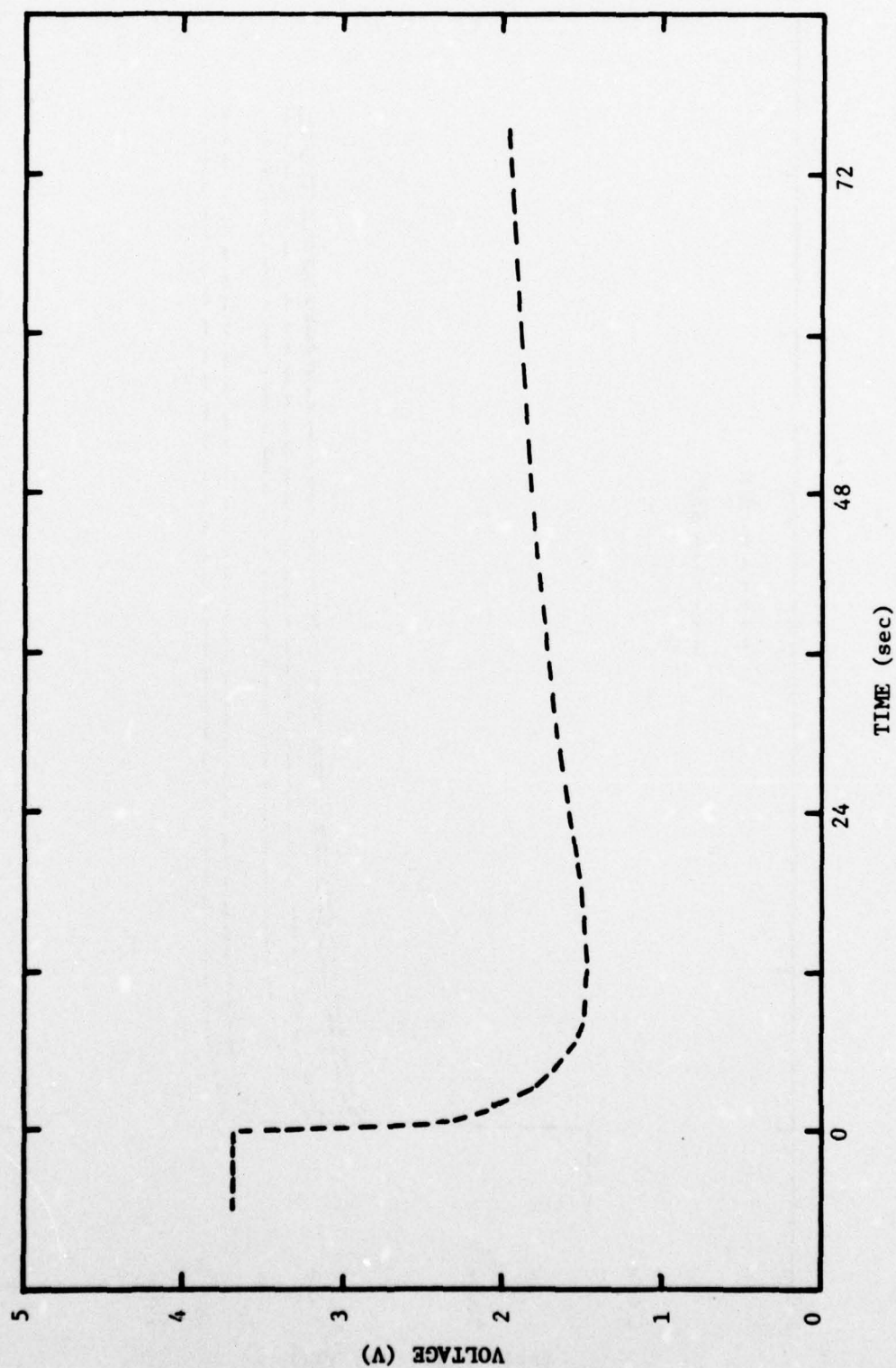


Fig. 8. Initial polarization of Li/SOCl₂ cell stored 287 hrs at 71°C. The cell was spiral wound with an anode area of 135 cm². The load was 4.6Ω.

the 4 cm² cells it is 3.0 cm⁻¹. In the multiple-plate cells, the ratio was 5.8 cm⁻¹ and in the spiral wound cells it was 17 cm⁻¹, comparable to a practical D cell. Thus it is probable that the insoluble materials which form the passivating film reach saturation in the electrolyte at a later time in the 1 cm² anode cells than in the others. Although the passivating film formation rate is sufficient to cause some reduction in cell performance of the 1 cm² cells, the rate of film dissolution is still sufficient to reduce the overall thickness.

B. The Effect of Exmet Anode Screen

In order to test the effect of the presence of the Exmet anode screen on cell performance, 1 cm² and 4 cm² anode quartz plate cells were prepared, stored at 71°C and tested under constant load. The results indicate that the Exmet makes a substantial difference in the 1 cm² anode cell behavior but not in the 4 cm² anode cell.

Figure 9 contains the initial discharge curve for six 1 cm² anode cells in which the anodes were pressed onto Ni Exmet. Comparing these data with those of 1 cm² anode cells without Exmet stored a similar length of time (see Fig. 2), we see a significant change in performance. The cells with Exmet exhibit behavior more comparable to the larger electrode cells, with an early voltage minimum followed by a gradual increase in cell voltage. The average current density at 60 sec was 5.06 mA/cm² or 73% that of fresh cells. The 1 cm² anode cells without Exmet discharged at an average of 5.86 mA/cm². Figure 10 contains the initial discharge curves for 4 cm² anode cells with Ni Exmet anode screens. These were stored 262 hrs at 71°C. The general pattern of the discharge is similar to the 1 cm² cells with Exmet and the larger area cells without Exmet. There is a minimum in each case followed by a gradual rise. In one cell, it was a sharp minimum, in the other two broad minima. The average current density at 60 sec was 5.25 mA/cm² or 76% of that of fresh cells. This compares with 4.91 mA/cm² observed with the cells without Exmet. Tests were conducted for longer storage times with similar results.

These data demonstrate that the presence of Exmet has a major effect on the performance of cells with 1 cm² anodes and a smaller effect on the 4 cm² anode cells. The evidence is clear in the case of the 1 cm² anodes, both by comparison of the curve shapes and by the current density at 60 sec. In the case of the 4 cm² anode cells with Exmet, the current density at 60 sec is actually greater than those without, but the shape of the curve is suggestive of the curves obtained from the relatively highly passivated cells. Thus we conclude there is some small effect of the Exmet on the 4 cm² cells.

The increased passivation observed in cells with Exmet anode screens is probably due to enhanced corrosion of the Li. The exposed portion of the Ni screen will be at the Li potential and thus be a site for SOCl₂ reduction. This would of course enhance the rate of Li dissolution. Evidently, such

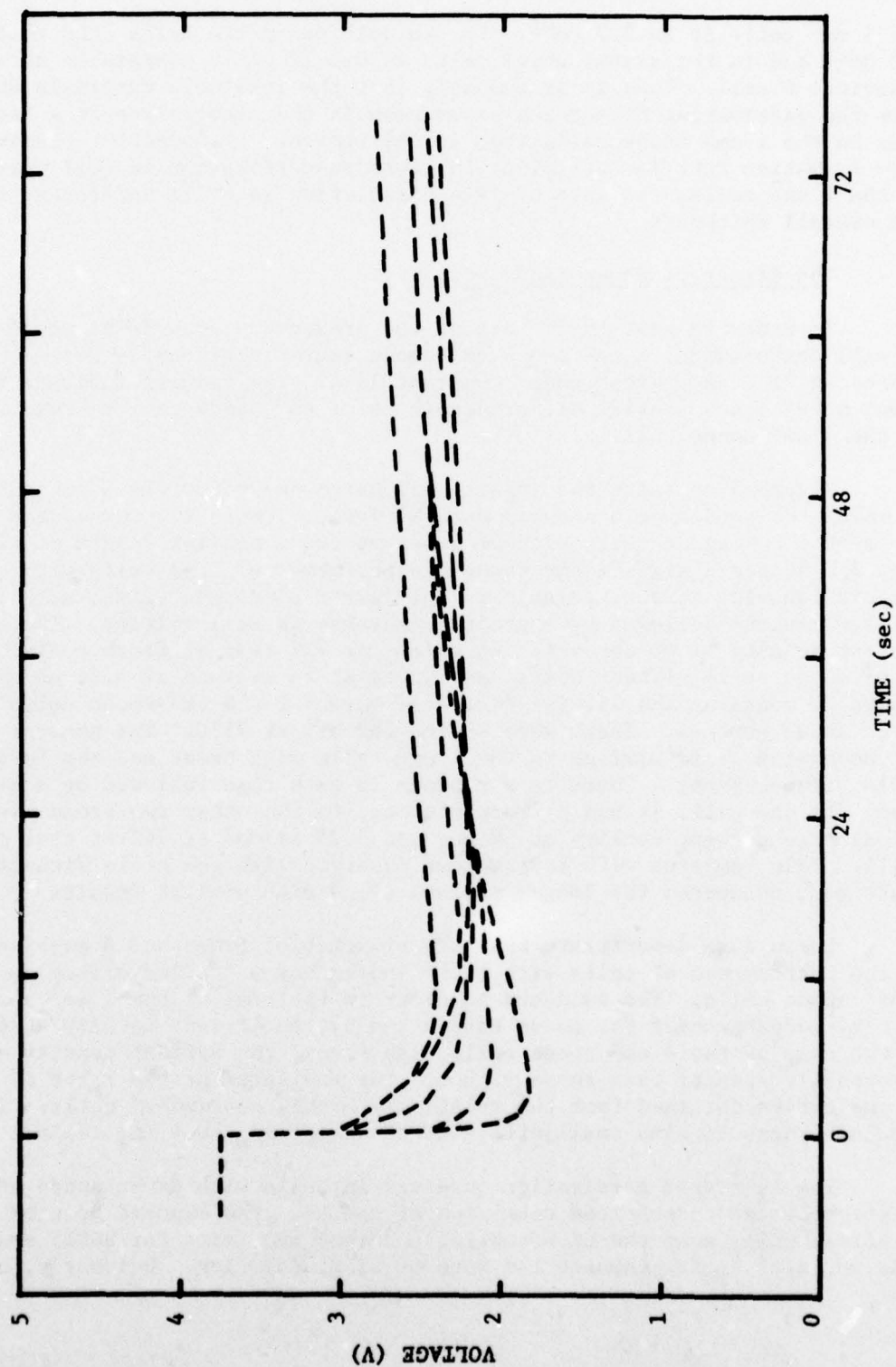


Fig. 9. Initial polarization of Li/SOCl₂ cells stored 257 hrs at 71°C. The anodes were 1 cm² with Exmet. The load was 490Ω.

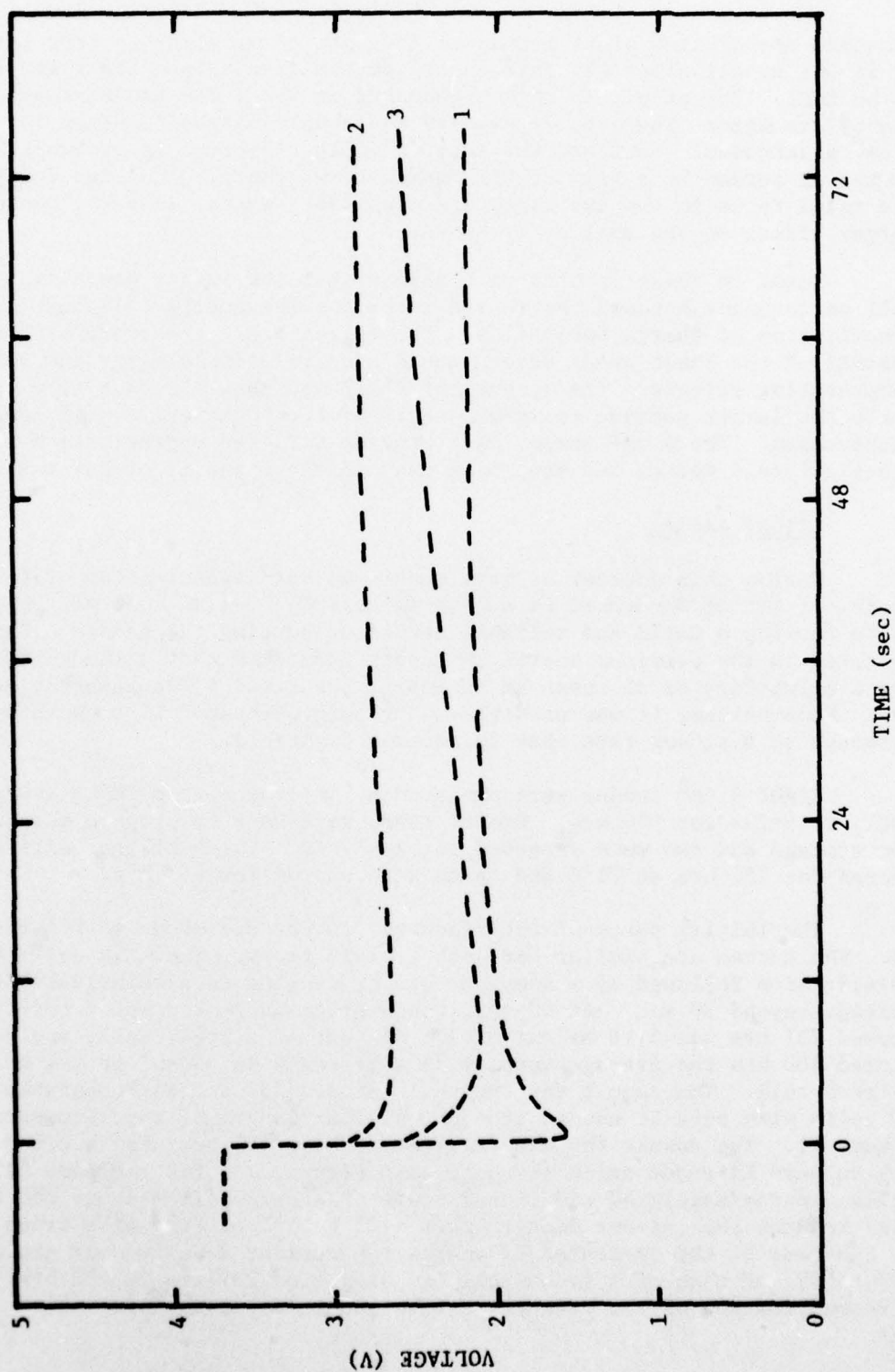


Fig. 10. Initial polarization of Li/SOCl₂ cells stored 267 hrs at 71°C. The anodes were 4 cm² with Exmet. The load was 121Ω.

enhanced dissolution of Li increases the rate of passivating film buildup. It is not at all clear why this should be the case, since the film is thought to be LiCl. The effect is more pronounced on the 1 cm² anode simply by virtue of its size: The area of exposed Ni is only slightly larger for the 4 cm² electrodes. Further, the rate of SOCl₂ reduction is probably limited on the Ni screen by a film of LiCl which forms there. Thus, we suspect that the total rates in the two cases are comparable which, in turn, causes a larger effect on the smaller Li anode.

Based on these results we conclude that the larger positive effect on cell performance between the Teflon cells and the quartz cells are due to the substitution of quartz for Teflon. The larger 4 cm² electrode area and the removal of the Exmet anode screen would have relatively minor and somewhat compensating effects. The removal of the Exmet should reduce film buildup, while the larger surface to volume ratio of the 4 cm² cells will enhance passivation. The 4 cm² anode cells provide a closer approximation to the practical cell design and have been used in the majority of our tests.

C. Li(Ca) Anodes

During this quarter we have continued our investigation of the beneficial effect of Ca-coated Li anodes in Li/SOCl₂ cells. One of the goals is to develop a rapid and reliable method of coating the anodes. Experiments reported in the previous quarterly report indicated that although Ca(SbCl₆)₂ has a solubility of at least 1M in SOCl₂, the free Ca⁺⁺ concentration is very low. Nonetheless, it was possible to prepare Ca-coated Li from this solution, although at a slower rate than is perhaps desirable.

Eight 4 cm² anodes were prepared by immersion in a 1M Ca(SbCl₆)₂/SOCl₂ solution for ~90 hrs. Six of these were used to prepare quartz cells for storage and two were reserved for analysis. Three of the cells were stored for 237 hrs at 71°C and three were stored for 480 hrs.

The initial parts of the discharge curves are shown in Figures 11 and 12. The curves are similar for both storage times. There is an initial rapid polarization followed by a somewhat slower decline to a relatively stable voltage beyond 30 sec. At 60 sec, the average current density for the cells stored 237 hrs was 5.18 mA/cm² or 74% of that of a fresh cell, and for cells stored 480 hrs the average current density was 4.86 mA/cm² or 69% of that of a fresh cell. The result for the cells stored 237 hrs is comparable to that of cells with pure Li anodes stored a similar length of time (compare with Figure 3). The result for the cells stored for 480 hrs show a clear superiority to pure Li anode cells (compare with Figure 7). For the pure Li anode cells, approximately 30 additional hours of storage (from about 250 to 280 hrs) reduced the current density from ~70% to 53% of that of a fresh cell. In the case of the Ca-coated Li anodes the current density only dropped from 74% to 69% of that of a fresh cell, in going from 237 hrs to 480 hrs. This is a reconfirmation of the effects we have reported previously.

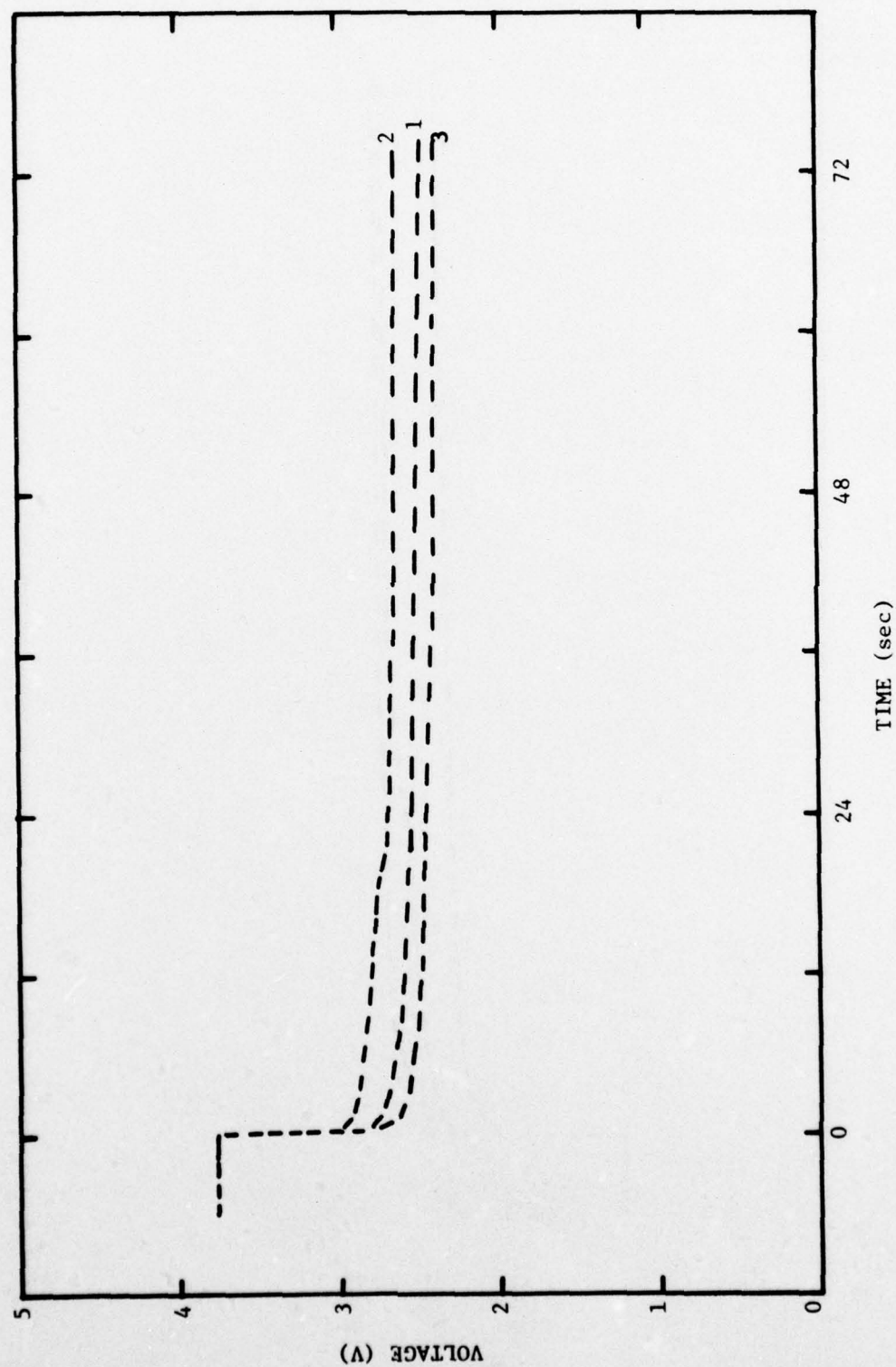


Fig. 11. Initial polarization of Li/SOCl₂ cells stored 237 hrs at 71°C. The anodes were Ca coated Li of 4 cm². The load was 121Ω.

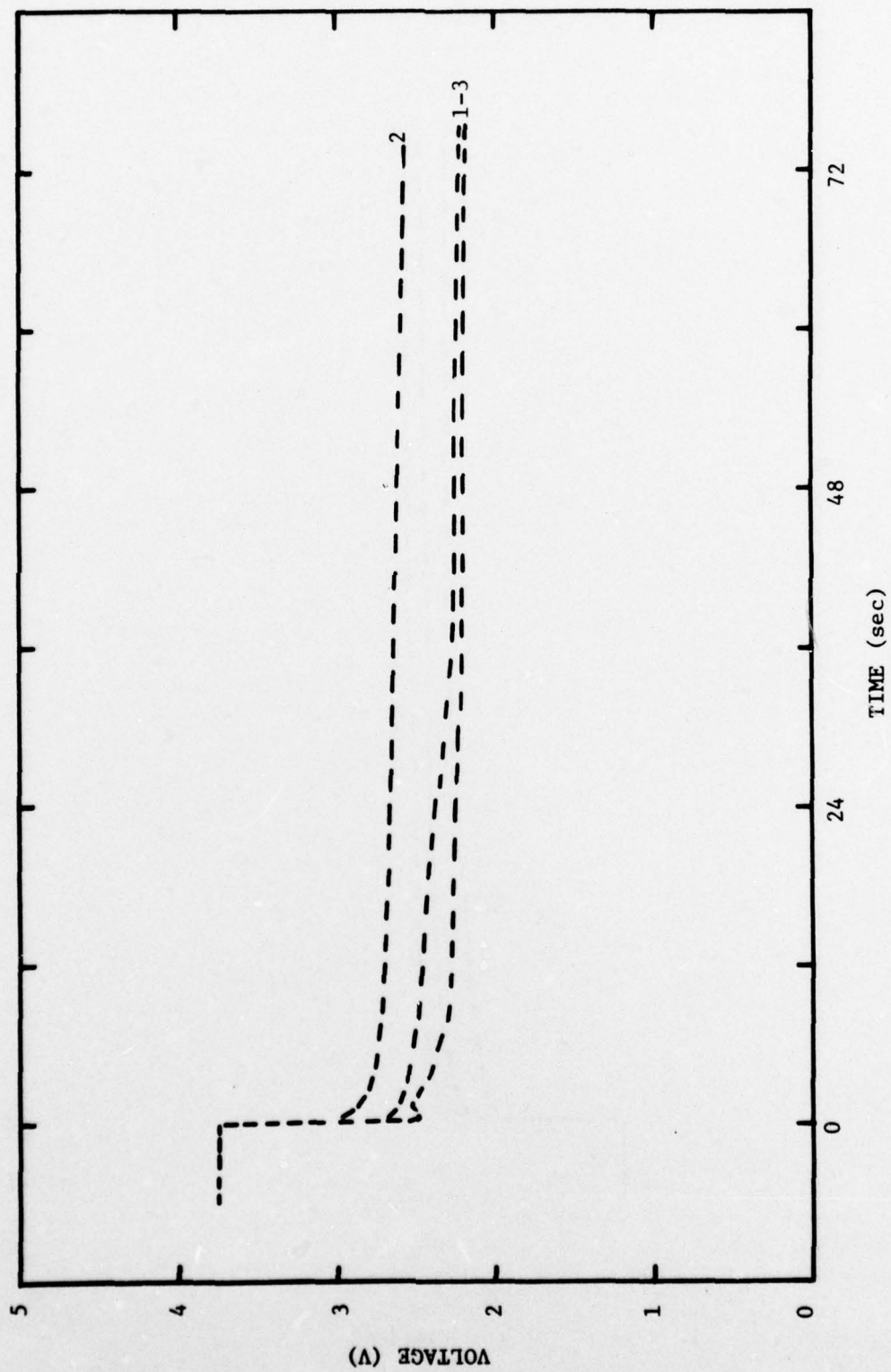


Fig. 12. Initial polarization of Li/SOCl₂ cells stored 480 hrs at 71°C. The anodes were Ca coated Li of 4 cm². The load was 121Ω.

The initial loss in cell performance is disconcerting in view of results we have obtained previously. We believe this loss is due to trace element contamination from the $\text{Ca}(\text{SbCl}_6)_2$ solution. The two Li anodes which were reserved were analyzed for Ca, Fe, Cu and Na by atomic absorption spectrophotometry. The samples were prepared by allowing the anodes to react with air overnight. Water was added continuously dropwise until any unreacted Li was consumed. The semisolid mass was dissolved with a few ml of conc. HCl and diluted to volume. The samples were analyzed with the AA using appropriate standards. The results were as follows: Ca, $51,000 \pm 1100$ ppm; Fe, 186 ± 14 ppm; Cu, 212 ± 6 ppm; Na, 206 ± 26 ppm. The Ca determination indicates the Ca deposited on the anodes was 2.8 coul/cm^2 . It is unlikely that this Ca remains as the pure metal. The Ca-Li binary phase data suggest that it is the compound Li_2Ca which is present. However, further investigation is necessary to establish this point. The Fe and Cu content of the anodes are substantial. The SbCl_5 used in preparing the $\text{Ca}(\text{SbCl}_6)_2$ solution is apparently the source of the contaminants. Previous analysis of the SOCl_2 and recent analysis of the CaCl_2 have shown that these contain insufficient Cu and Fe to account for the levels observed here. Iron is known to be detrimental to the storage capabilities of Li anodes. Thus, we suspect that the Fe contamination, and probably also the Cu contamination, are responsible for the initial loss in performance observed in these tests. What is very encouraging, however, is the retention of performance at the longer 480 hr storage times. It would seem that the contaminants exercise most of their detrimental effect during the initial phases of storage and have minor effects thereafter.

Further tests will be carried out with anodes prepared from $\text{Ca}(\text{SbCl}_6)_2$ solutions after these solutions have been purified of Fe and Cu. We will use the same technique for this as we use to purify the LiAlCl_4 electrolyte solutions. The $\text{Ca}(\text{SbCl}_6)_2$ solutions will be stored at 71°C with Ca metal. This treatment should eliminate the more noble Fe and Cu and other active contaminants.

D. The Effect of PCl_3 , PCl_5 and P_2S_5 Additives

During the present quarter we have tested the effect of three other additives on the performance of Li/ SOCl_2 cells after storage at 71°C . These were PCl_3 , PCl_5 and P_2S_5 . They were selected because they are known to stabilize SOCl_2 against thermal decomposition (9) and it may be that SOCl_2 is generated either by the thermal decomposition of the electrolyte or by electrolyte attack on the Li anodes. On this basis, it was felt that these additives could be of advantage. Electrolytes were prepared with 1 weight % (1 w/o) of PCl_3 (Fisher, reagent, P-110), PCl_5 (Eastman, pract. P-470) and P_2S_5 (Fisher, tech. P-108). Five quartz plate cells were prepared from each of these electrolytes. Three of each were stored for 280 hrs at 71°C and two of each were stored for 522 hrs. They were tested with a constant load which draws 7 mA/cm^2 from fresh cells.

No voltage delay was observed in any of the cells stored 280 hrs (Figures 13-15). After 522 hrs of storage, the PCl_3 and PCl_5 cells still had no voltage delay. The P_2S_5 cells did (Figures 16-18). The performance of the PCl_3 and PCl_5 cells is the best we have seen to date for non-Ca-coated anodes. The average current density for the PCl_3 cells after 280 hrs of storage was 6.34 mA/cm^2 at 60 sec or 90% of that of fresh cells. After 522 hrs of storage, the average current density was 5.52 mA/cm^2 at 60 sec or 79% of that of fresh cells. There is more scatter in the data of the PCl_5 cells, but nonetheless the average current density after 280 hrs of storage was 5.91 mA/cm^2 at 60 sec or 84% of that of fresh cells. After 522 hrs of storage, the current density was 5.72 mA/cm^2 at 60 sec or 81% of that of fresh cells. The P_2S_5 cells after 280 hrs of storage had an average current density at 60 sec of 5.99 mA/cm^2 or 85% of that of fresh cells. This performance degraded sharply at 522 hrs of storage to an average current density of 60 sec of 4.07 mA/cm^2 or 58% of that of fresh cells. The two of the P_2S_5 cells after 280 hrs storage had a sharp minima within the first few sec of discharge (Figure 15). The third had a suggestion of this. This may be indicative of film growth which eventually leads to severe passivation.

These test results for the PCl_3 and PCl_5 additives are encouraging. The mechanism leading to the improved performance is unknown for the moment. It may well be that these compounds are stabilizing reactive intermediates such as SCl_2 , thus preventing attack of the Li. An alternate mechanism is that they are acting as Cl^- acceptors. PCl_5 is known to be a Cl^- acceptor in some oxychloride systems (10), but there is no evidence that this is the case in the SOCl_2 solvent system. A complete discharge of one of the PCl_5 cells showed about 50% of the capacity of a fresh cell. Thus it seems possible that these compounds are solubilizing the passivating film and concurrently enhancing Li corrosion. The improved performance of the cells with these two additives (PCl_3 and PCl_5) seems to make a resolution of this question worthwhile.

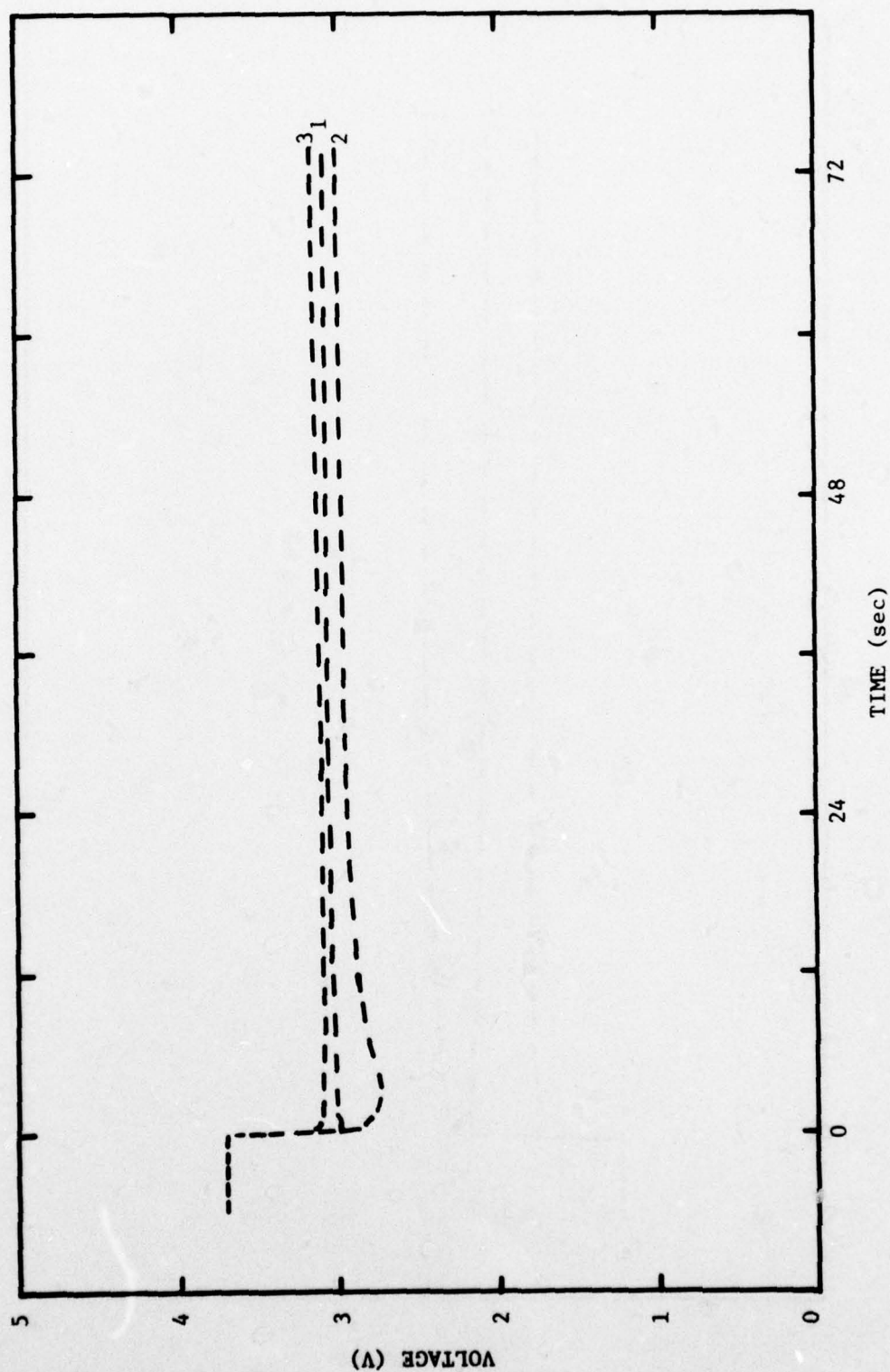


Fig. 13. Initial polarization of Li/SOCl₂ cells stored 280 hrs at 71°C. The anodes were 4 cm². The electrolyte contained 1 w/o PCl₃. The load was 121Ω.

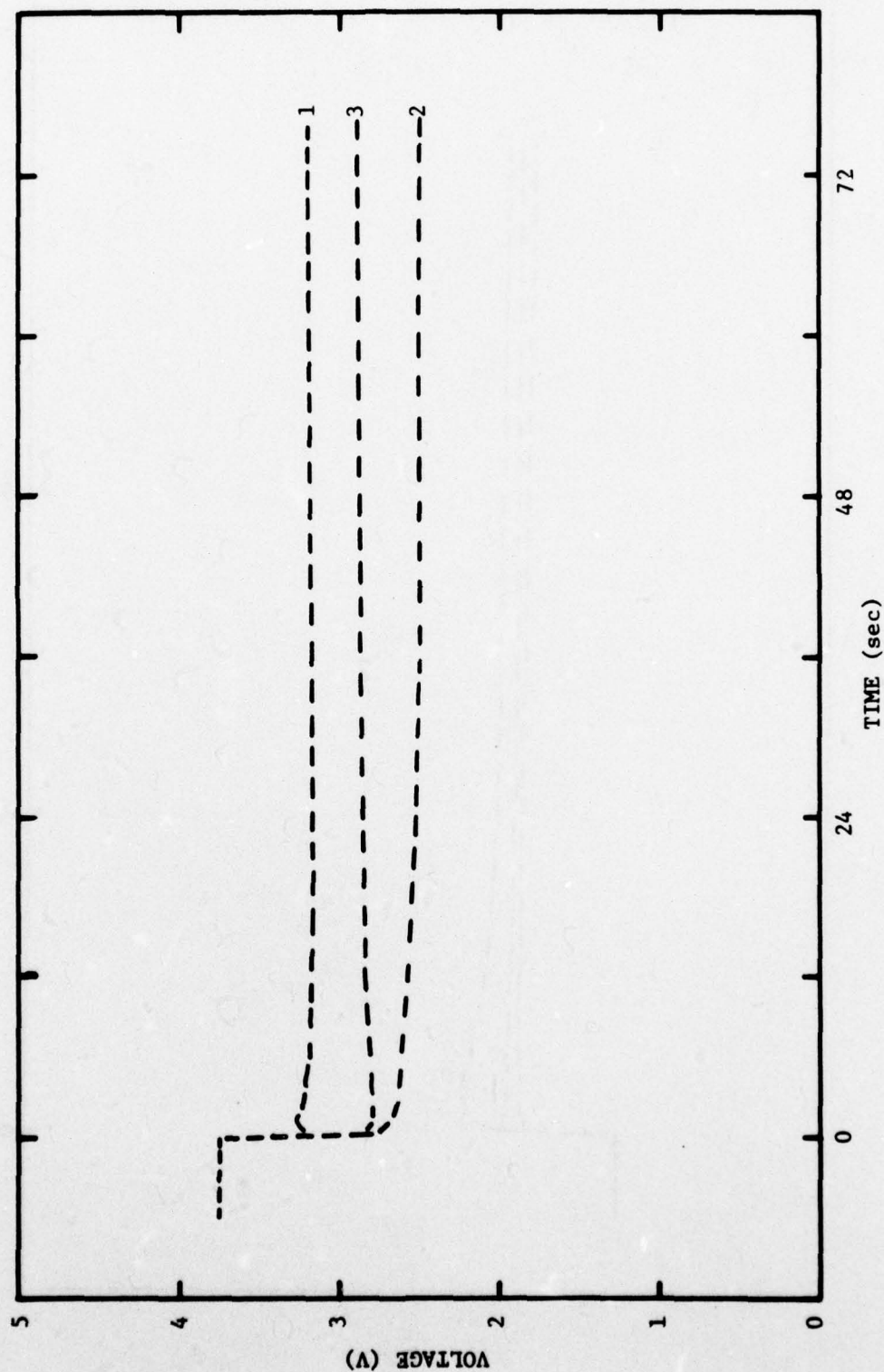


Fig. 14. Initial polarization of Li/SOCl₂ cells stored 280 hrs at 71°C. The anodes were 4 cm². The electrolyte contained 1 w/o PCl₅. The load was 121Ω.

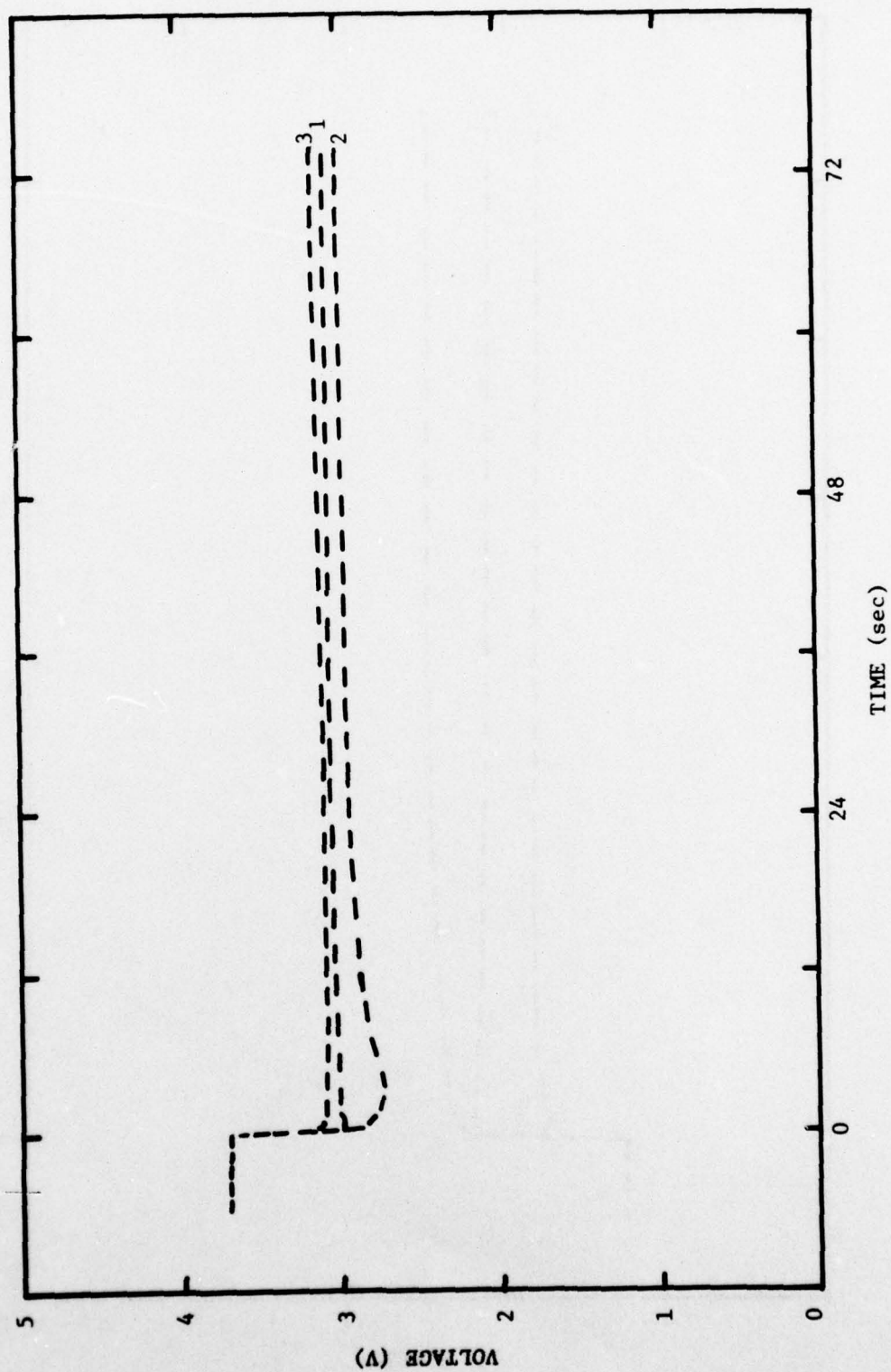


Fig. 13. Initial polarization of Li/SOCl₂ cells stored 280 hrs at 71°C. The anodes were 4 cm². The electrolyte contained 1 w/o PCl₃. The load was 121Ω.

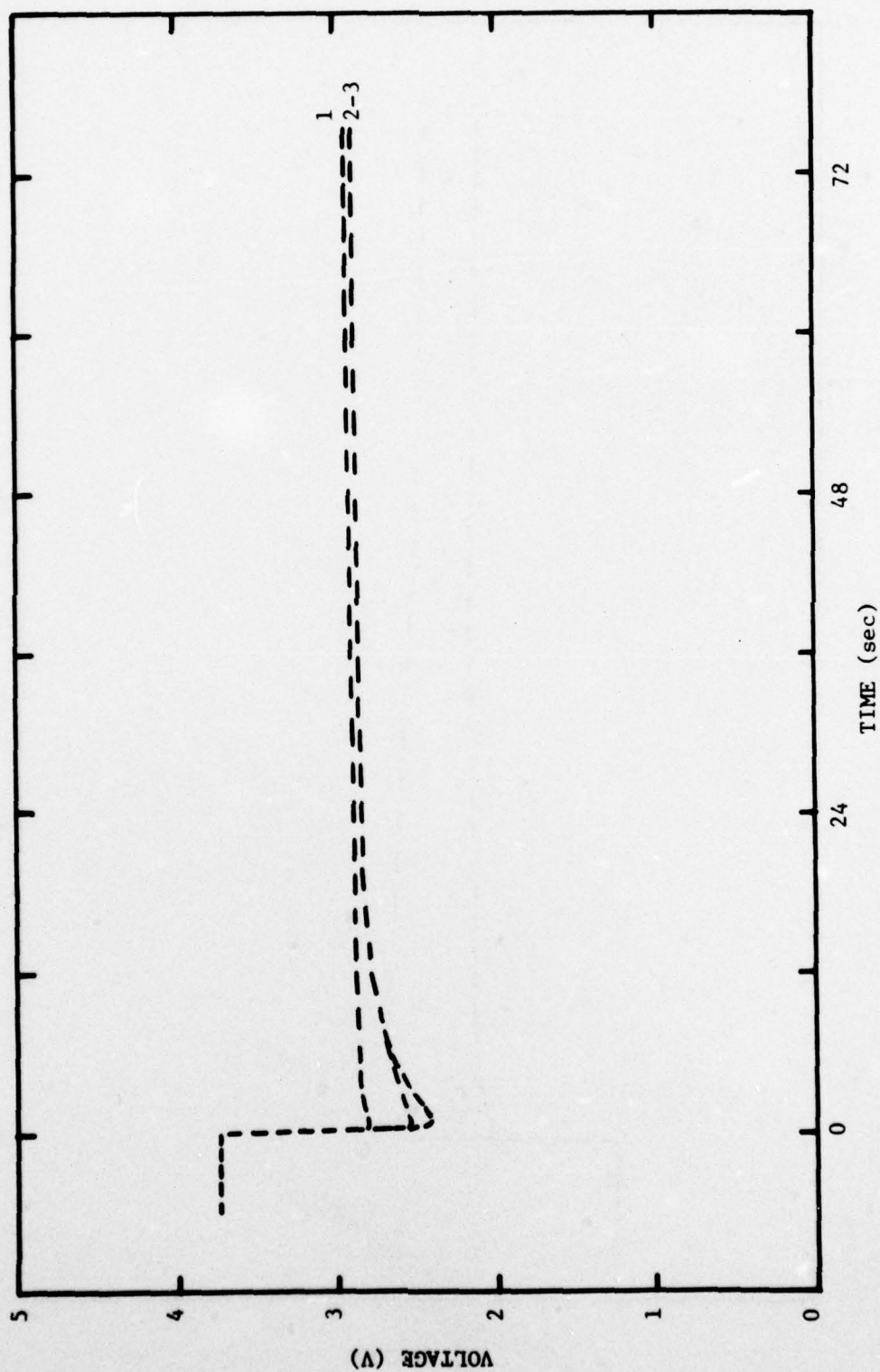


Fig. 15. Initial polarization of Li/SOCl₂ cells stored 280 hrs at 71°C. The anodes were 4 cm². The electrolyte contained 1 w/o P₂S₅. The load was 121Ω.

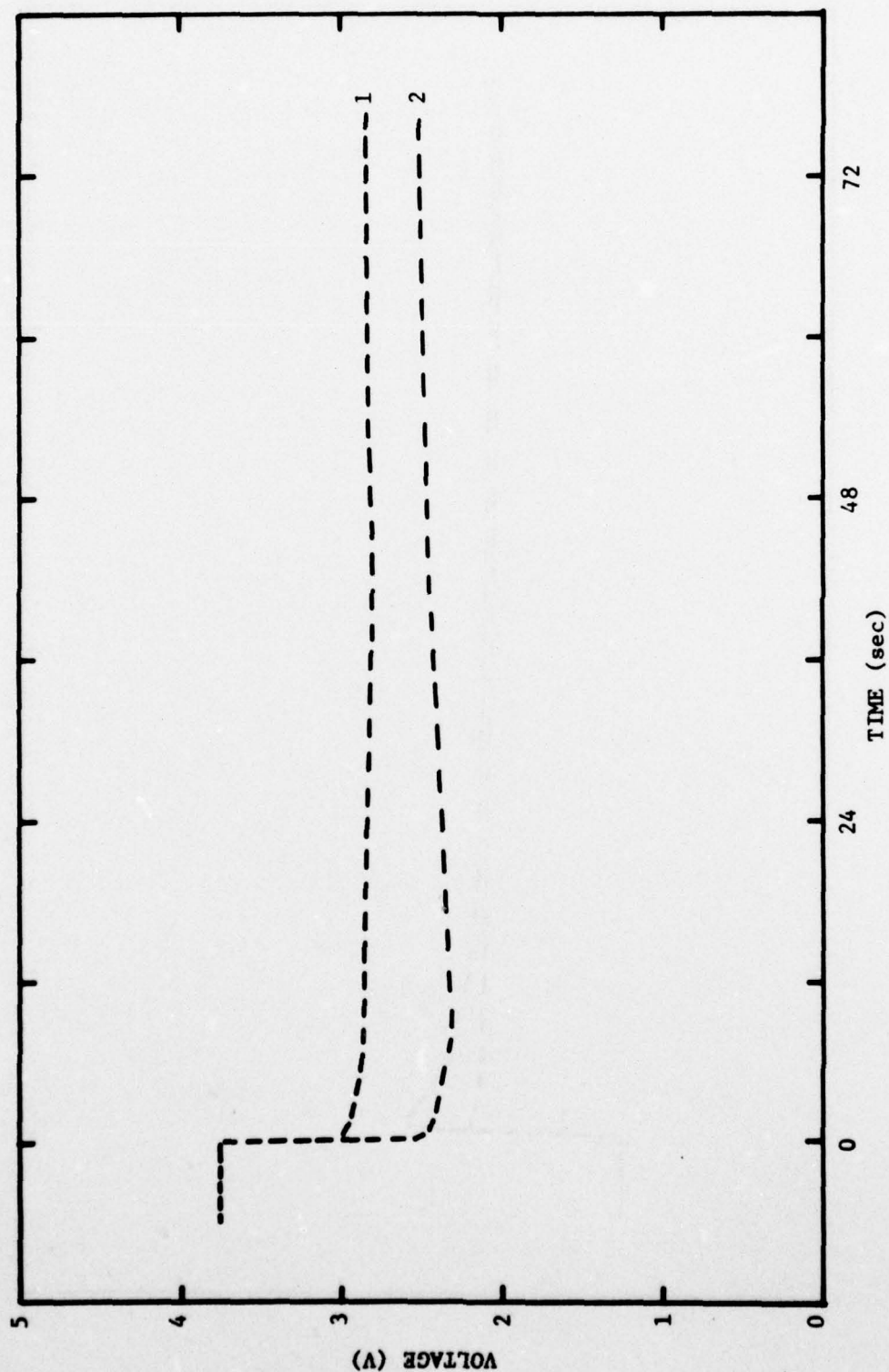


Fig. 16. Initial polarization of Li/SOCl₂ cells stored 522 hrs at 71°C. The anodes were 4 cm². The electrolyte contained 1 w/o PCl₃. The load was 121Ω.

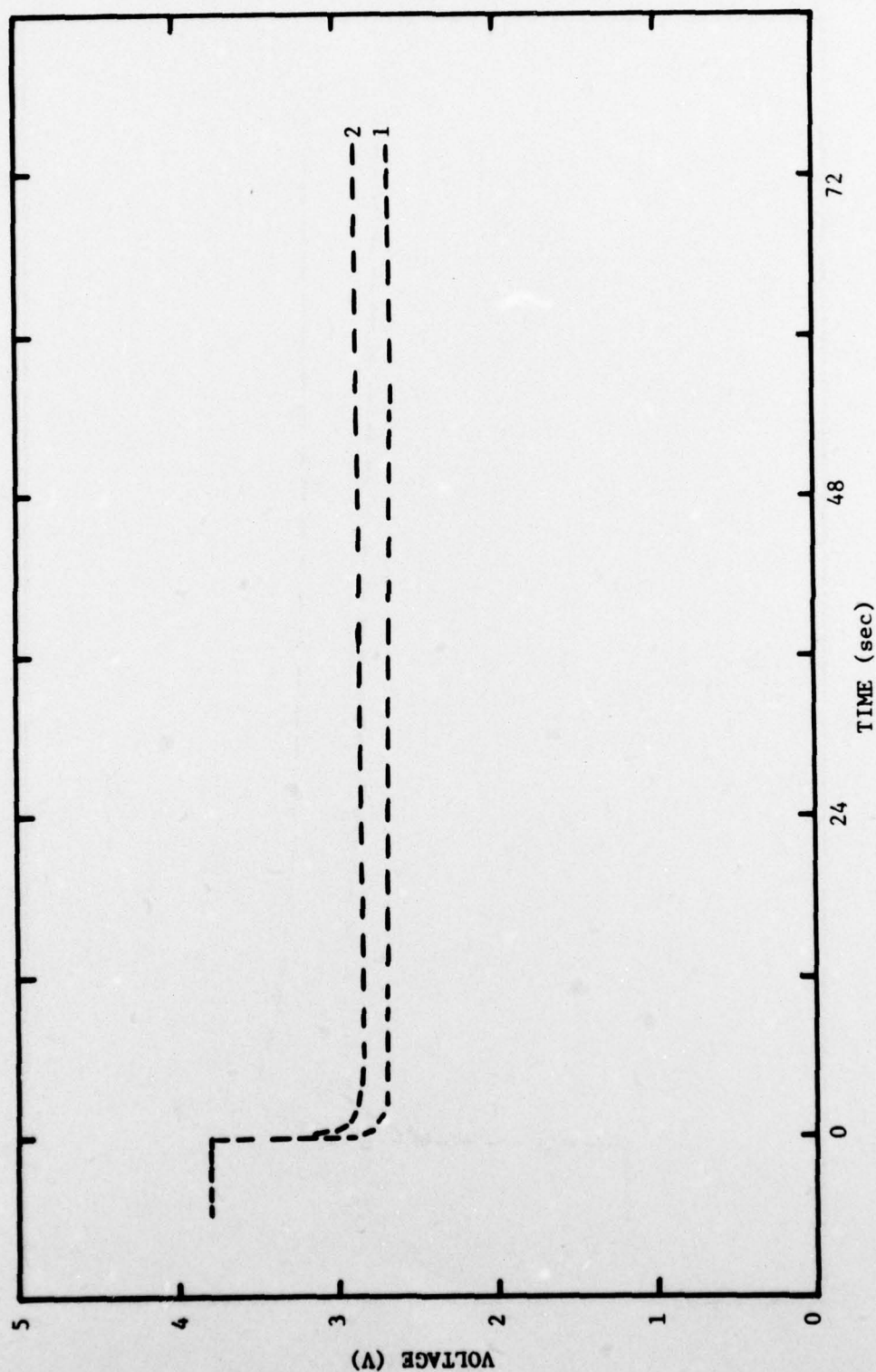


Fig. 17. Initial polarization of Li/SOCl₂ cells stored 522 hrs at 71°C. The anodes were 4 cm². The electrolyte contained 1 w/o PCl₅. The load was 121Ω.

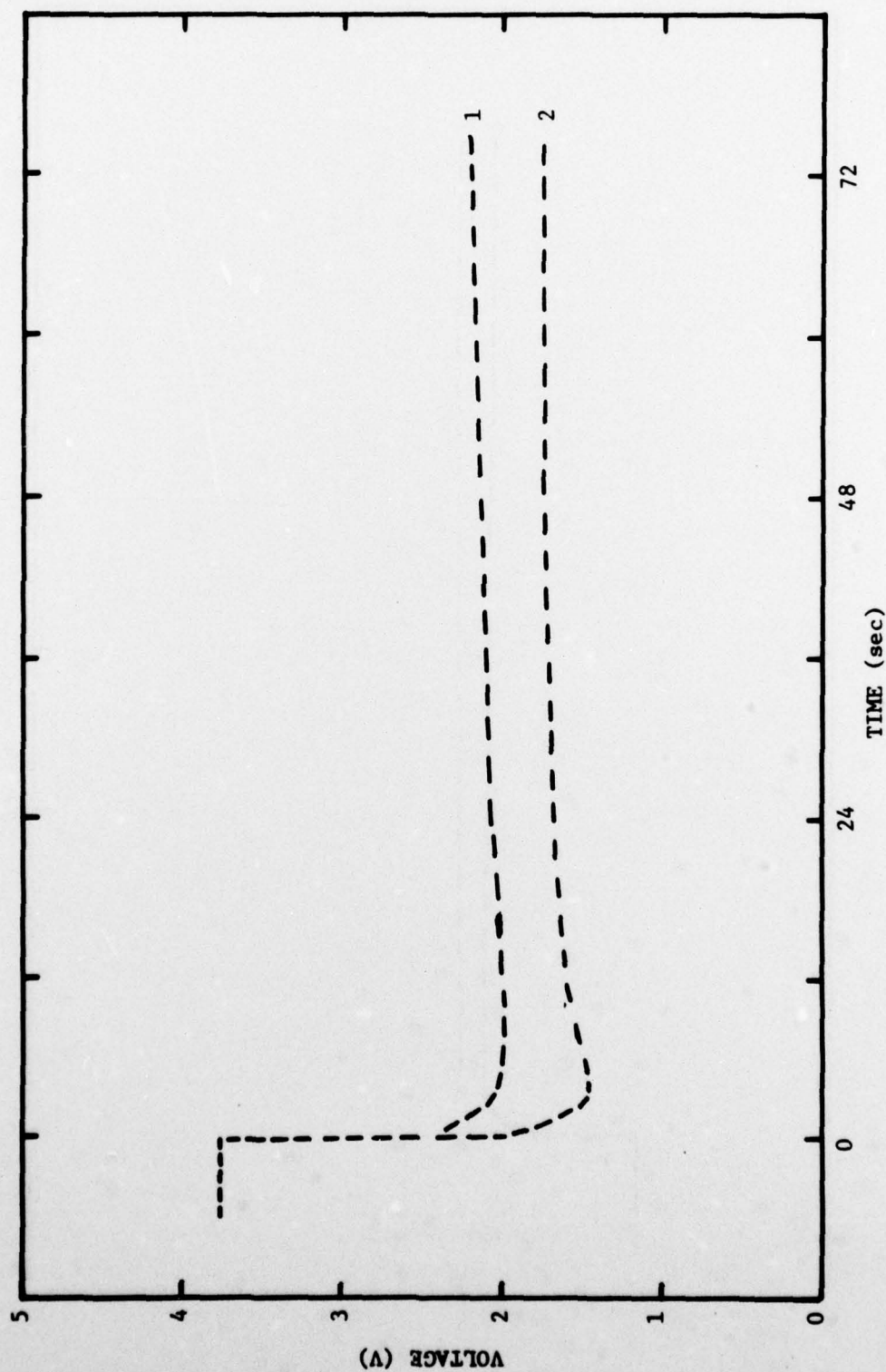


Fig. 18. Initial polarization of Li/SOCl₂ cells stored 522 hrs at 71°C. The anodes were 4 cm². The electrolyte contained 1 w/o P₂S₅. The load was 121Ω.

III. INFRARED SPECTROPHOTOMETRY

An investigation of SOCl_2 -based electrolyte systems by infrared spectrophotometry has been continued. The ultimate aim is to provide a more complete understanding of the chemistry of the system and to evaluate the usefulness of the IR method for analysis. Particularly important areas to be explored are the electrolyte purity, discharge reaction products, and solution decomposition products. In the previous quarterly report we established that pretreatment of the 1.5M $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte removes hydroxyaluminum compounds and HCl , increases the SO_2 content, and introduces some new species which has an absorption band at $\sim 1060\text{ cm}^{-1}$. During this quarter we have looked more thoroughly at the effects on the IR spectrum of electrolyte storage with Li. We have also examined the spectra of two inorganic ions, SO_3^- and $\text{S}_2\text{O}_4^{2-}$ in SOCl_2 .

A. Experimental

Spectra were recorded on a Beckman Acculab 5 dual beam spectrophotometer. The instrument covers the mid-IR range from 4000 cm^{-1} to 375 cm^{-1} . All of the spectra reported here were obtained with Beckman TAC cells. These have AgCl windows and are completely sealable. Two path lengths have been used, 0.025 mm and 0.1 mm. Cell-filling operations were carried out in an argon filled glove box.

B. Effects of Storage with Li

The basic results observed and reported in the previous quarterly report have been confirmed. The 1.5M $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte after preparation and before storage (Figure 19) with Li shows IR bands at $\sim 3320\text{ cm}^{-1}$ indicative of O-H stretching (probably from hydroxyaluminum compounds) at 1313 cm^{-1} (indicative of SO_2) and an unidentified peak at 685 cm^{-1} . After 44 hrs of storage at 71°C with Li (Figure 20), the bands at 3320 cm^{-1} and 685 cm^{-1} disappear from the spectra. Bands appear at 2750 cm^{-1} and 1060 cm^{-1} . The 2750 cm^{-1} band is indicative of HCl . The band at 1060 cm^{-1} is still unidentified but is probably due to some S-O containing compound. A large number of such compounds have absorbances in this region (11,12). The SO_2 band also increases. After 205 hrs of storage (Figure 21), the 3320 cm^{-1} and 685 cm^{-1} bands are still absent. The HCl band at 2750 cm^{-1} has diminished by a factor of 3 and the band at 1060 cm^{-1} has remained unchanged. After 330 hrs of storage, the HCl band is reduced further and again the 1060 cm^{-1} band remained unchanged.

These data indicate that the hydroxyaluminum compounds react readily with Li to produce HCl . This HCl subsequently reacts, but more slowly, with

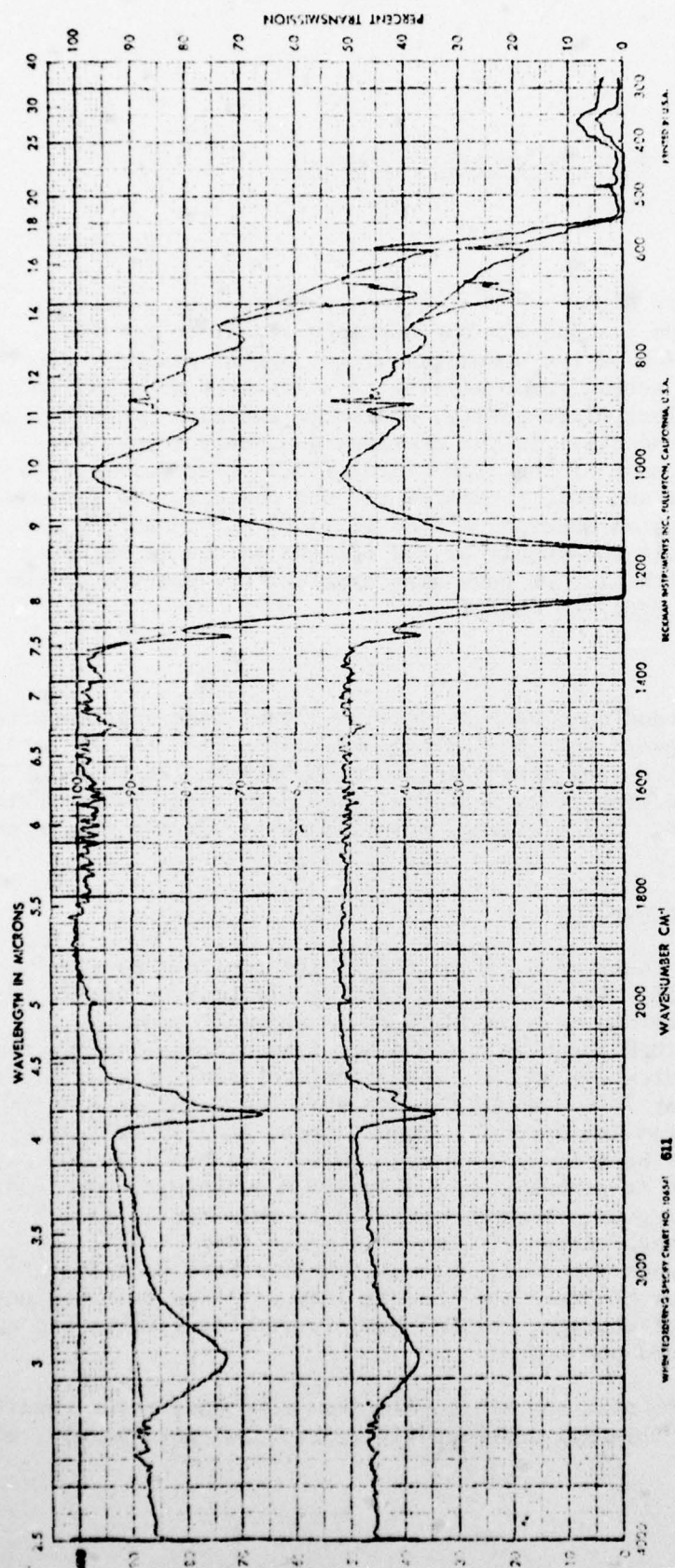


Fig. 19. Infrared spectrum of 1.5M $\text{LiAlCl}_4/\text{SOCl}_2$ before pretreatment with Li.

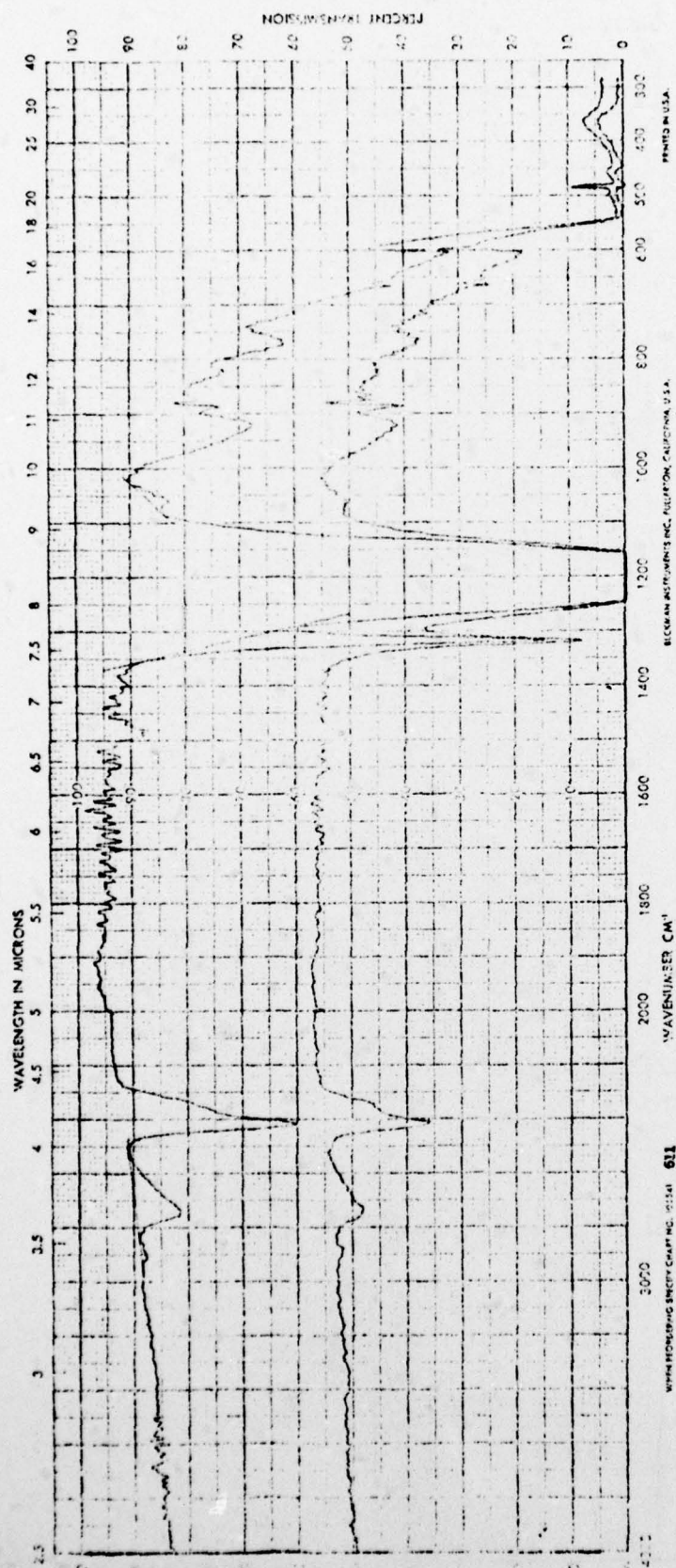


Fig. 20. Infrared spectrum of 1.5M $\text{LiAlCl}_4/\text{SOCl}_2$ after 44 hrs at 71°C with Li.

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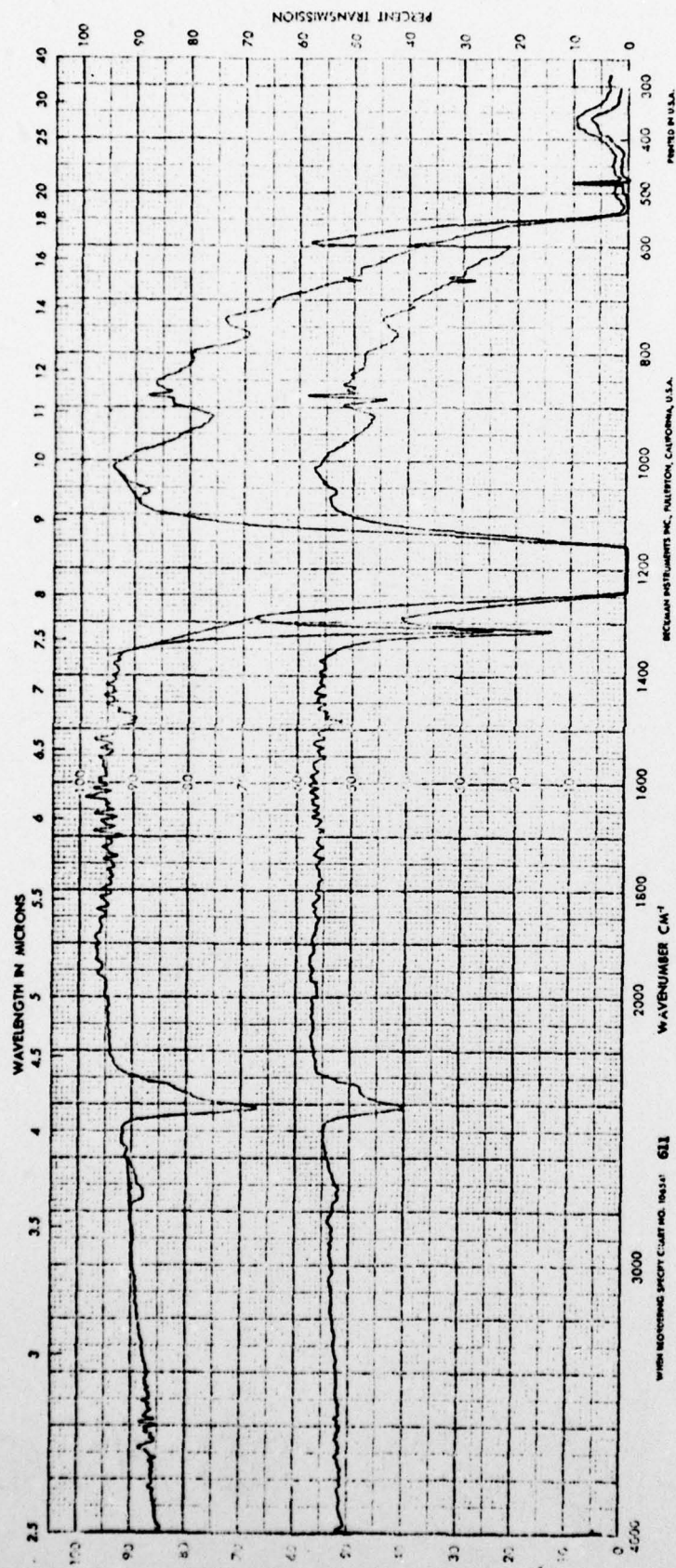


Fig. 21. Infrared spectrum of 1.5M $\text{LiAlCl}_4/\text{SOCl}_2$ after 205 hrs at 71°C with Li.

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the Li. The exact reaction mechanism is unclear, but must involve the hydroxy compound, Li and SOCl_2 . The SOCl_2 must be involved because a direct reaction between only the Li and the hydroxy compounds would most likely produce H_2 and not HCl . Thus it must be a Li-mediated reaction between the SOCl_2 and the hydroxy compounds. SOCl_2 and these compounds do not react directly at any appreciable rate because the 3320 cm^{-1} band has been observed to be stable for at least 3 weeks at room temperature.

The disappearance of the 685 cm^{-1} band along with the 3320 cm^{-1} suggests they may be related. It is possible that this band may be due to Al-O stretching. This needs further confirmation.

C. IR Spectra of SO_3^- and S_2O_4^-

We attempted to obtain the IR spectra of SO_3^- and S_2O_4^- in SOCl_2 solution. This was both to identify the IR band at 1060 cm^{-1} and to increase our library of data for analytical use. Quantities of the Na^+ salts of these two anions were placed in tubes with SOCl_2 . After several days at room temperature, IR spectra were obtained of the solutions. Neither salt dissolved completely. Indeed, there was little evidence of any dissolution. In the container with the Na_2SO_3 there was no change in the SOCl_2 . The solution with $\text{Na}_2\text{S}_2\text{O}_4$, however, had become yellow. An aliquot of this solution was brought to dryness. A yellow solid remained which we identified as S. It had a melting point of $114-117^\circ\text{C}$, melted to a dark red liquid and burned with a blue flame. The burning material had a pungent odor. Apparently, S_2O_4^- reacts with SOCl_2 , probably acting as a reducing agent. The IR spectrum of this solution showed a massive increase in SO_2 over that of SOCl_2 . The IR spectrum of the SO_3^- solution showed no changes from pure SOCl_2 . In neither case was a band at 1060 cm^{-1} observed. Thus, neither of these species is responsible for this band in the electrolyte solutions.

IV. SUMMARY AND FUTURE WORK

During the past quarter we have continued to work on the voltage delay problem suffered by Li/SOCl₂ cells during storage. We have identified that the substitution of Teflon by quartz in our cell design is the major source of improvement observed in these cells. We have also established the anode size and the presence or absence of Ni Exmet grid influence the severity of electrode passivation. Electrodes of 1 cm², which have a relatively small surface-to-volume ratio, retain better discharge characteristics after storage at 71°C than do larger electrodes. This may be indicative of a surface film dissolution process wherein the volume of electrolyte reaches saturation of species forming the soluble film at shorter times with high surface to volume ratio electrodes.

The presence of Ni Exmet anode screen seems to enhance the Li anode passivation process. The effect is more pronounced on the 1 cm² anodes than on the 4 cm² anodes. It appears that exposed Ni acts as a surface for the reduction of SOCl₂. This enhances the passivation rate. It is not at all clear why this should be the case if the passivating film is LiCl, as is commonly supposed. The effect is more dramatic with 1 cm² electrodes probably because the total rates of SOCl₂ reduction on the Ni tabs are not very much different between the 1 cm² and 4 cm² anodes, so the rate of film thickening is thereby reduced on the larger electrodes.

Li(Ca) anodes prepared from 1M Ca(SbCl₆)₂/SOCl₂ solutions show good retention of resistance to passivation for storage times up to 480 hrs. There is, however, a significant initial passivation, which is probably due to co-deposition of Fe and Cu contaminants with the Ca. We feel that removing these contaminants before the preparation of the Li(Ca) anodes will eliminate this initial passivation.

Storage tests with PCl₃, PCl₅ and P₂S₅ have indicated PCl₃ and PCl₅ at 1 w/o concentration in the electrolyte may be beneficial in reducing cell passivation during storage. They may however be acting as Cl⁻ acceptors and causing additional corrosion of the Li anode. More tests are necessary to establish this point.

IR spectrophotometry has indicated that hydroxy compounds introduced into the electrolyte during preparation are removed after 44 hrs of storage with Li at 71°C. This process generates HCl which is subsequently removed by longer storage times (~300 hrs). The mechanism of HCl generation is unclear. It appears that the HCl must arise from a Li-mediated reaction between the hydroxy compounds and SOCl₂.

The SO_3^- and S_2O_4^- anions have limited solubility in SOCl_2 and are not detectable in the IR. S_2O_4^- apparently reacts with SOCl_2 at room temperature, producing SO_2 and S.

During the next quarter we will continue to explore the problem of voltage delay. Li(Ca) anodes will be prepared from purified $\text{Ca}(\text{SbCl}_6)_2$ solutions and tested. Experiments aimed at determining film growth rates and film composition will be initiated. Further tests with PCl_3 and PCl_5 additives are also indicated.

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